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[Jour. Indian Chem. Soc., Vol. 30, No. 9, 1953]

ALUMINIUM ALKOXIDES

By R. C. Mehrotra

A general method for the preparation of higher alkoxides of aluminium has been described. The molecular weights of aluminium ethoxide, isomeric propoxides and butoxides have been accurately measured in boiling benzene. The variation in the degree of association of the isomeric alkoxides is explained in terms of the steric hindrance due to branched alkoxide groups. A probable structure for these alkoxides is proposed. The boiling points of the alkoxides are measured over a range of pressure and they are found to satisfy the relationship '$\log p = a - b/T$' and from the equation, the molar latent heat and the entropy of vaporisation at 5.0 mm. pressure are calculated.

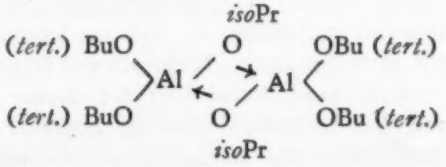
The alkoxides of aluminium are generally prepared by the action of an alcohol on aluminium (Gladstone and Tribe, *J. Chem. Soc.*, 1881, **39**, 4; Tischtschenko, *J. Russ. Phys. Chem. Soc.*, 1899, **31**, 694, 784). The method requires a large excess of the alcohol and, even with the help of a catalyst, it is extremely slow in some cases, e.g., *tert.*-butanol. The action of aluminium alkoxides with other alcohols has been mentioned by Tischtschenko (*loc. cit.*) and Adkins and Cox (*J. Amer. Chem. Soc.*, 1938, **60**, 1151). Baker (*ibid.*, 1938, **60**, 2673) studied the action of organic esters with aluminium *iso*propoxide.

In the present investigation, a new general method has been described for the preparation of higher alkoxides of aluminium; it consists in refluxing under a column aluminium *iso*propoxide in benzene with the higher alcohol, the *iso*propanol produced being removed azeotropically with benzene:

$$Al(OPr^i)_3 + 3\,ROH \longrightarrow Al(OR)_3 + 3\,Pr^iOH.$$

Tri-*n*-propoxide, *n*-butoxide, and *sec.*-butoxide of aluminium were prepared by the above method in quantitative yield. The main advantages of the method are: (1) a small excess of the alcohol and (2) a quantitative yield. However, on attempting to prepare *tert.*-butoxide by the above method, it was found that the replacement of the first *iso*propoxide group occurred quite readily, but the speed of replacement of the second *iso*propoxide group was slow while that of the third did not appear to proceed at all even when the *iso*propanol produced was continuously removed (cf. Baker, *loc. cit.*).

The molecular weight of aluminium *iso*propoxide di-*tert.*-butoxide in boiling benzene showed it to be a dimer, and the most probable structure that can be assigned to the compound is:



The shielding effect of the tertiary groups sterically hinders the co-ordination of another molecule of tertiary butanol. Bradley, Mehrotra and Wardlaw (*J. Chem. Soc.*,

1952, 4204), in their attempt to prepare zirconium *tert.*-butoxide from zirconium methoxide, observed that zirconium mono-methoxide tritertiary butoxide was the end product. As is to be expected, the reaction between tertiary butanol and aluminium ethoxide is found to be slightly less hindered than with *iso*propoxide. Further, it has been shown that in the reaction of aluminium ethoxide with *tert.*-butyl acetate, two of the ethoxide groups are readily replaced while the third is removed quite slowly.

The results of earlier workers on the boiling point and molecular weight of aluminium alkoxides show wide variations, and so a careful redetermination of these was undertaken. The boiling points of the alkoxides were measured at several pressures between 0.1 and 10. 0mm. mercury and in all cases, the data fitted straight lines of the form '$\log p_{mm.} = a - b/T$' in the pressure range of 2 to 10 mm. The values for the constants 'a' and 'b' are listed in Table I along with the boiling points (under 5.0 mm. pressure), latent heats of vaporisation (L_v, k-cal. mole^{-1}) and entropies of vaporisation at 5 mm. pressure ($\triangle S_{5.0}$ cal. mole^{-1} degree^{-1}).

TABLE I

Alkoxide.	$t_{5.0}°$.	a.	b.	L_v.	$\triangle S_{5.0}$.	M.W.	X.
$Al(OEt)_3$	184.5	11.8	5100	23.9	52.2	663	4.1
Al (O *n*-Pr)$_3$	232.5	12.6	6025	27.5	54.5	818	4.0
Al (O *iso*Pr)$_3$	124.0	11.4	4240	19.4	48.9	610	3.0
Al (O *n*-Bu)$_3$	270.0	12.7	6540	29.9	55.0	962	3.9
Al (O *sec.*-Bu)$_3$	172.0	11.3	4720	21.6	48.5	580	2.4
Al (O *tert.*-Bu)$_3$	—	—	—	—	—	480	1.95

The molecular weights of the alkoxides were measured ebullioscopically in benzene by a modified Menzies' method (*J. Amer. Chem. Soc.*, 1921, **43**, 2309) and are given in the seventh column of the table. The molecular weight was determined with freshly distilled samples of the alkoxides and the figures given above are the average of five to six determinations with increasing concentration. In no case, a noticeable effect of concentration of the solution was found on the measured molecular weight. The last column shows the degree of association (X) in boiling benzene. The molecular weight of freshly distilled aluminium *iso*propoxide was also measured in boiling *iso*propanol, and it was found to be trimeric also in *iso*propanol.

The molecular weights of some aluminium alkoxides have been measured cryoscopically in benzene by Ulich and Nespital (*Z. physikal. Chem.*, 1933, **165**, 294) and also by Robinson and Peak (*J. Phys. Chem.*, 1935, **39**, 1125). The latter workers found that aluminium ethoxide, propoxides, *n*- and *sec.*-butoxides all showed a tetrameric molecular weight in naphthalene. McElvain and Davie (*J. Amer. Chem. Soc.*, 1951, **73**, 1400), on the other hand, found that the degree of association of aluminium *iso*propoxide and *tert.*-butoxide in boiling benzene were 5-6 and 1.9 respectively, whereas in camphor at the melting point, the molecular weight of aluminium ethoxide was double of the formula weight and aluminium *tert.*-butoxide behaved as a monomer.

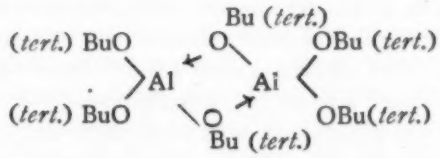
The variations in the results of the earlier workers might be due to ageing effect on the alkoxides. The hydrated oxide of aluminium is well known to show marked ageing effect and the phenomenon has also been observed (Mehrotra, Ph. D. Thesis, London University, 1952) in the case of zirconium ethoxide. Therefore, the molecular weight of aluminium *iso*propoxide was redetermined after keeping it in a dry atmosphere for two months when it exhibited an association nearly corresponding to tetrameric form in boiling benzene, whereas the same sample on redistillation showed a trimeric nature.

The degree of association of the isomeric butoxides of aluminium decreases from 4 in the case of *n*-butoxide to 2 in the case of *tert.*-butoxide. Similar relationships have been found for zirconium alkoxides.

TABLE II

Alkoxide.	$T_{5\cdot0}°$.	a.	b.	L_v.	$S_{5\cdot0}$.	M.W.	X.
$Zr(OEt)_4$	234.8	13.7	6600	30.2	59.4	980	3.6
$Zr(O\ iso\text{-}Pr)_4$	203.8	15.2	6895	31.5	66.0	967	3.0
$Zr(O\ tert.\text{-}Bu)_4$	89.1	9.90	3330	15.2	42.0	381	1.0

It has been established (Bradley, Mehrotra and Wardlaw, *J. Chem. Soc.*, 1952, 2027, 4204, 5020) that steric factors play an important part in determining the structure and volatility of the alkoxides of titanium and zirconium. The powerful shielding of the central atom by branched alkoxide groups prevents strong intermolecular bonding in the tertiary alkoxides which have been shown to be monomeric. However, as shown above, aluminium *tert.*-butoxide though less associated than the *n*- or *sec.*-butoxide is still dimeric. The following structural formula is suggested for the compound :



in which each aluminium atom is surronnded by only four *tert.*-butyl groups and so should be sterically possible (atomic radii of Al, Ti and Zr atoms are 1.26, 1.36 and 1.48 Å respectively). The above structure is similar to the one accepted for the dimeric aluminium halides where the stability of the bridge structure is shown by its existence even in the vapour phase.

EXPERIMENTAL

All-glass apparatus fitted with interchangeable joints was used throughout and special precautions were taken to exclude moisture. In the alcoholysis experiments, fractionation was carried out in a column (30 inches) packed with Fenske helices and fitted to a total-condensation variable take-off stillhead.

Aluminium was in the form of turnings. Benzene (Analar) was dried over sodium and redistilled. *tert.*-Butyl alcohol (B.D.H., Lab. reagent) was dried over calcium oxide followed by distillation over sodium *tert.*-butoxide. Other alcohols were dried by usual procedures and were finally purified by careful fractionation.

Analytical Methods.—Aluminium was determined by dissolving the alkoxide in hydrochloric acid and precipitating and weighing as oxinate.

Ethoxide and *iso*propoxide were determined by a back titration method (Bradley and Wardlaw, *J. Chem. Soc.*, 1950, 3450). For the analysis of ethoxide and *iso*propoxide in the presence of *tert.*-butoxide, it was found that *tert.*-butanol did not interfere in the above method of estimation, if the reaction mixture was kept in a cool place.

Molecular Weights.—The conventional Menzies-Wright ebulliometer was modified according to Dr. D. C. Bradley, London University (*private communication*), so that a weighed quantity of the solvent could be employed. The apparatus consisted of a double walled glass cylinder with a bulb of nearly 20 c.c. capacity at the lower end. At the upper end, the outer cylinder was fitted with a socket (B24) through which could be suspended the differential water thermometer which also was joined to a B24 through cone. Near the top, the outer cylinder was connected to a condenser which had a through B14 cone at the lower end so that the rate of reflux could be controlled. The upper end of the condenser had a B24 socket for holding the Wright pippette. The conventional type Cottrell's lift pump was employed for ensuring that the temperature of the lower bulb was in equilibrium with the solution.

In an experiment, about 15 g. of the solvent was taken in the bulb. The whole apparatus was surrounded by a tubular draught shield. The liquid was heated with a very small flame and care was taken to ensure that the rate of refluxing was uniform in all observations by counting the drops of the solvent dripping from the lower end of the condenser. After the usual preliminary measurements, successive additions of the solute were made, and each elevation recorded was the mean of five or six closely agreeing readings. The elevations (ΔT) were plotted against the weight of the solute (m) and in all cases, a straight line was obtained. The apparatus constant (for 100 g. of the solvent) was determined using azobenzene and was found to be 29.56 for benzene and 16.00 for *iso*propanol. The results are recorded in the table below.

TABLE III

Alkoxide.	No. of determns.	Range of m.	Benzene.	Molecular weight. Found.	Calc.
Al (O Et)$_3$	3	0.023-0.164 g.	16.37 g.	660	162.2
Al (O *iso*-Pr)$_3$	5	0.311-1.212	15.00	610	204.2
Al (O *n*-Pr)$_3$	5	0.717-1.512	15.93	818	204.2
Al (O *n*-Bu)$_3$	8	0.239-2.016	15.52	962	246.2
Al (O *sec.*-Bu)$_3$	4	0.310-1.071	15.71	580	246.2
Al (O *tert.*-Bu)$_3$	4	0.179-0.763	15.00	480	246.2
Al (O *tert.*-Bu)$_2$ (O *iso*-Pr)	5	0.166-0.618	15.55	460	232.2
Al (O *iso*-Pr)$_3$ (aged for 2 months)	6	0.160-1.024	15.76	782	204.2
Al (O *iso*-Pr)$_3$	4	0.312-1.592	13.38 (*iso*propanol)	621	204.2

Boiling Points.—A special all-glass apparatus was prepared for the measurement of boiling points over a range of pressures. It consisted of a flask (about 15 c.c.) joined through a semi-micro Claisen head to a total condensation variable take-off stillhead. Thus boiling points under conditions of total reflux were measured and the purity of the alkoxide could be ascertained by collecting fractions. The rate of reflux, diameter of the capillary leak, and the temperature difference between heating bath and boiling point observed were carefully controlled to be the same in each experiment. A mercury Vacustat reading from 0.01 to 10.0 mm. was employed for reading the pressure in the system.

Aluminium ethoxide was prepared by the method of Chalmers ("Org. Synthesis", 1935, Vol. **15**, p. 182). A yield of 80% was obtained. The product was purified by distillation and 90% of the product distilled over at 162°-163°/1.3 mm. [Found : Al, 16.71 ; EtO, 83.4. Calc. for Al $(OEt)_3$: Al, 16.63; EtO, 83.37 per cent]. Boiling points : 162°/1.3 ; 169°/1.5 ; 171°/2.2 ; 181°/4.2 ; 184°/5.0 ; 188°/6.0 ; 190°/6.8 ; 194°/8.5 and 197°/10.0 mm.

Aluminium iso*propoxide* was prepared as described by Young, Hartung and Crossley (*J. Amer. Chem. Soc.*, 1936, **58**, 100). The yield obtained was 85% and 90% of the product distilled at 94°/0.5 mm. [Found : Al, 13.22 ; *iso*-PrO, 87.0. Calc. for Al (O *iso*-Pr)$_3$: Al, 13.20 ; *iso*-PrO, 86.8 per cent]. Boiling points : 106°/1.5 ; 111°/2.3 ; 113°/2.5 ; 118°/3.8 ; 122°/4.6 ; 124°/5.2 ; 125.5°/5.5 ; 131°/7.5 ; 132°/8.3 ; 135°/10.0 mm.

Aluminium n-*propoxide* was prepared by the alcohol interchange of aluminium *iso*propoxide with *n*-propanol in the presence of benzene. Aluminium *iso*propoxide (12.0 g.) in benzene (60 c.c.) and *n*-propanol (12 g., b.p. 97.2°/755 mm.) was refluxed at 150°-160° under a column. About 30 c.c. of benzene-*iso*propanol azeotrope was collected at 71° and then some liquid was collected between 73° and 78°. Finally, the temperature of the distilling liquid rose to 80° when benzene was distilled off at a low reflux ratio to remove any traces of *iso*propanol being produced. From the product, benzene was removed by distillation under reduced pressure and a clear colorless liquid distilled at 205° under 1.0 mm., yield 11.5 g. of the distilled product. [Found : Al, 13.24. Calc. for Al(O *n*-Pr)$_3$: Al, 13.20 per cent]. Boiling points : 205°/1.0 ; 211°/1.9 ; 214°/1.9 ; 215°/2.0 ; 221.5°/3.0 ; 228°/4.0 ; 233°/5.0 ; 234°/5.2 ; 238°/6.9 ; 239.5°/7.5 ; 243°/9.0 ; 245°/10.0 mm.

Aluminium n-*butoxide*—To aluminium *iso*propoxide (10.2 g.) in benzene (60 c.c.) was distilled *n*-butanol (13.3 g., b.p. 117.5°/755 mm.) and the mixture was refluxed at bath temperature of 140°-150°. Alcohol interchange was complete within half an hour and then the remaining benzene was distilled off at a high reflux ratio. The product was distilled under reduced pressure using a capillary leak when 13.0 g. of a clear colorless liquid distilled at 235° under 0.3 mm. pressure. [Found : Al, 10.99. Calc. for Al (O *n*-Bu)$_3$: Al, 10.95 per cent]. Boiling points : 242°/0.7 ; 258°/2.7 ; 262°/3.6 ; 272°/6.0 ; 276°/7.5 ; 281°/8.8 ; 284°/10.0 mm.

Aluminium sec.-*butoxide* was prepared by the alcohol interchange of aluminium ethoxide (11.3 g.) with *sec.*-butyl alcohol (18.2 g., b.p. 99°/750 mm.) in

the presence of benzene (60 c.c.). The alcohol interchange was slower than with *n*-butyl alcohol. About 30 c.c. of benzene-alcohol azeotrope was collected at 68°-70° after which the reaction became quite slow and the remaining ethanol was removed by distilling benzene at a high reflux ratio (25:1). The total time required was 6 hours. Finally, benzene was distilled off at 80°. The product was distilled at 183° under 9.0 mm. pressure when a clear colorless liquid (16.2 g.) was obtained. [Found : Al, 10.91. Calc. for Al $(OBu)_3$: Al, 10.95 per cent]. Boiling points : 134°/0.25; 151°/1.3 ; 156°/2.0 ; 164°/3.5 ; 170°/4.6 ; 173°/5.7 ; 177°/6.6 ; 181°/8.0 ; 185°/10.0 mm.

Alcohol Interchange of Aluminium iso*propoxide with* tert.-*Butyl Alcohol.*—To aluminium *iso*propoxide (23.4 g.) was distilled *tert.*-butanol (66.2 g., b.p. 82.5°/745 mm.) and benzene (135 g.). The mixture was refluxed under a column (60 cm. long filled with Fenske helices) at a bath temperature of 140°. Distillate at 72°-74° was collected at a reflux ratio of 25:1 for 26 hours when the temperature of the distillate began to rise. About 30 c.c. of benzene was then distilled off at a high reflux ratio and the clear solution in the flask on being allowed to stand overnight deposited beautiful transparent crystals. The benzene was removed by distillation under reduced pressure and the white powder obtained was analysed. (Found : Al, 11.56 ; *iso*-PrO, 45.0 ; *iso*-PrO : Al, 1.76). Evidently, the product is a mixture of Al (O *iso*-Pr)-(O *tert.*-Bu)$_2$ and Al (O *iso*-Pr)$_2$ (O *tert.*-Bu) in the molar ratio of 1 : 3.

The white powder (24 g.) obtained above was again treated with *tert.*-butanol (41 g.) and benzene (123 g.). The distillate at 72°-73° was collected at a high reflux ratio, and finally the benzene was distilled. Total time of refluxing was 28 hours. From the colorless solution thus obtained, benzene was removed under reduced pressure and the white powder obtained was dried at 70°-80° under 0.1 mm. pressure for one hour. (Found : Al, 11.71 ; *iso*-PrO, 20.5 ; *iso*-Pr O : Al, 0.81). The powder was next sublimed. It sublimed readily at a bath temperature of 100°-105° under 0.2 mm. pressure. The crystalline white sublimate was analysed. [Found : Al, 11.57 ; *iso*-PrO, 25.2. Al (O *iso*-Pr) (O *tert.*-Bu)$_2$ requires Al, 11.61 ; *iso*-Pr O, 25.45 per cent].

Alcohol Interchange of Aluminium Ethoxide with tert.-*Butyl Alcohol.*—Aluminium ethoxide (4.9 g.) was taken in *tert.*-butanol (30 g.) and benzene (40 c.c.) and the mixture was refluxed under the column at a bath temperature of 140°-150°. The distillate was collected at 70°-73° under a high reflux ratio of 1:25 and finally the solvent was distilled off slowly. The product crystallised out from the clear solution on cooling. The clear mother-liquor was decanted off and the solid was sublimed at a bath temperature of 170°-180° under 0.2 mm., yield 4.2 g. of a white solid. [Found : Al, 11.95 ; EtO, 13.8 ; EtO : Al, 0.70.) A mixture of Al(OEt) (O*tert.*-Bu)$_2$ and Al (O *tert.*-Bu)$_3$ in the molar ratio of 2:1 requires Al, 11.85 ; EtO, 13.3 per cent].

Alcohol Interchange of Aluminium Ethoxide with tert.-*Butyl Acetate.*—Aluminium ethoxide (6.1 g.) was refluxed in dry *tert.*-butyl acetate (47 g.) at a bath temperature of 150°-160° under a column. Some distillate (about 5 g.) was collected at 77°-79° during 5 hours' refluxing and then distillate at 80°-85° was collected at a high reflux ratio when the temperature finally rose to 95° and remained constant for

3 hours. The solvent was then distilled off at a high reflux ratio. The substance had not dissolved completely in the solvent even towards the end of the reaction. The product was dried for 6 hours at room temperature under 0.1 mm. giving 8.8 g. of a white powder which was sublimed at 140° under 0.1 mm. pressure yielding 7.9 g. of a crystalline powder. [Found : Al, 11.57 ; EtO, 9.3%. A mixture of (OEt) (O *tert.*-Bu)$_2$ and Al (OBu)$_3$ in equimolecular ratio requires Al, 11.61 and EtO, 9.7 per cent].

Aluminium tritertiary butoxide was prepared according to the method of Wayne and Adkins ("Org. Synthesis", 1941, Vol. **21**, p. 8), The product was purified by subliming twice at 160°/1 0 mm. [Found : Al. 10.97. Calc. for Al(O *tert.*-Bu)$_3$: Al, 10.95 per cent].

Most of the experimental work was carried out at Birkbeck College, London University. The author is deeply grateful to Prof. W. Wardlaw and Dr. D. C. Bradley for their kind interest and encouragement and to the British Council for a fellowship.

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FERRIC COMPLEXES OF PHENOLS. PART I. PHENOL, *m*-CRESOL

By S. K. K. Jatkar and B. N. Mattoo

Colorimetric titration of $FeCl_3$ with phenol at (M/400 Fe^{3+}) shows the existence of the complex $Fe(OR)^{2+}$, which is shown by the calculation of the instability or equilibrium constant. At higher concentrations, (M/100 Fe^{3+} and M/15 Fe^{3+}), Job's method of continuous variation shows the existence of $Fe(OR)^{2+}$ and $Fe(OR)_3$ respectively, in case of phenol and *m*-cresol.

The potentiometric study of these reactions at higher concentrations, using platinum as the indicator electrode, shows the existence of the whole series of complex $Fe(OR)_n^{3-n}$, where $n = 1, 2, 3 \ldots 6$.

The colour of the complexes is explained quantitatively as due to the frequency difference between various ultraviolet and visible absorption frequencies of the constituent chromophores.

Ferric chloride reaction with phenols, giving rise to various colorations, violet, blue or red, is widely used as a qualitative test of the aromatic hydroxyl group. Possible structures have been proposed by Weinland and Binder (*Ber.*, 1912, **45**, 148, 2948) and Claasz (*Arch. Pharm.*, 1915, **253**, 360). The former postulate the presence of such acids as $H_3[Fe'''(C_6H_4O_2)_3]$ and $H[Fe'''(C_6H_4O_2)_2]$ in case of catechol. In Et_2O solution they isolated compounds of the type $(Cl_2.Fe\text{-}O\text{-}C_6H_4OH).Et_2O$ and it was suggested that similar compounds were formed with other phenols. Claasz (*loc. cit.*) postulated the formation of the salt $Fe(OC_6H_5)_3$ in case of phenol.

Brode and Wesp (*J. Amer. Chem. Soc.*, 1934, **56**, 1037) from a spectrophotometric study of the ferric-phenol colours, concluded that it was the ferric ion only that took part in the reaction and not the negative radical of the ferric salt. They postulated structure $Fe(OR)_6^{3-}$, where $-OR$ is the ionised phenol. The colour was found to be more intense in solvents which caused more dissociation of phenols

Taylor (*Virginia J. Sci.*, 1942, **3**, 24) and Babko (*J. Gen. Chem. U. S. S. R.*, 1945, **15**, 874) postulate $Fe(OR)^{++}$ structure for the ferric complexes of phenols.

Harvey Jr. and Manning (*J. Amer. Chem. Soc.*, 1950, **72**, 4488) showed the existence of three complexes FeR_1, FeR_2, FeR_3 in case of disodium 1:2-dihydroxybenzene-3 : 5-disulphonate, indicating that Fe^{3+} could combine with 2, 4 and 6 phenolate groups. Babko (*J. Gen. Chem. U. S. S. R.*, 1945, **15**, 745) similarly reports three complexes FeR'_1, FeR'_2 and FeR'_3 in case of salicylic acid.

Banerjee and Halder (*Nature*, 1950, **165**, 1012) found evidence for $Fe(OR)_3$ and $Fe(OR)_6^{3-}$ by thermometric and conductometric methods, but by the absorption method they obtained indication of $Fe(OR)_3$ alone. They found no evidence for complexes $Fe(OR)_n^{3-n}$ where n is less than 3 ; $3\text{-}n$ being the charge on the complex. It has been definitely shown in the present work that these lower complexes do exist. The method of continuous variation shows $Fe(OR)_3$ complex at higher concentrations only. The position of the maxima, and hence, the nature of the complex is not independent of concentration as reported by Banerjee and Halder (*loc. cit.*). The variation curves at lower concentration give definite maxima at 1 : 2 (Fe : PhOH) and the curves are independent of wave-length. The presence of $Fe(OR)^{++}{}_1$ has also been established by a colorimetric titration at a very low concentration.

EXPERIMENTAL

Aqueous solutions of $FeCl_3$ and phenols were used. The $FeCl_3$ solutions were standardised by reduction and subsequent oxidation by $K_2Cr_2O_7$ using diphenylamine as the indicator. Dilute solutions when required were freshly prepared from stock $FeCl_3$ (0.1*M*) solution. The phenol solution was standardised by brominating with $KBrO_3$-KBr-HCl. Excess of Br was estimated iodimetrically. In case of *m*-cresol, Kahlbaum A. G. quality was used after distilling it to remove traces of moisture absorbed during storage.

Absorption measurements were made on a Klett-Sommerson photoelectric colorimeter and the E. M. F. measurements on a Doran D. C. potentiometer.

Ferric Chloride-Phenol

Job's Method of Continuous Variation.—The method (Job, *Ann. chim.*, 1928, *x*, **9**, 113; Vosburgh and Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437) was used to study the reaction at different concentrations, viz., *M*/15; *M*/30 and *M*/100. Equimolar solutions of the reactants were mixed in varying proportion and absorption (R) of the resulting solution measured. The absorption (r) calculated for the mixture, had there been no reaction, is subtracted from the value R. The difference 'Y' ($R-r$) was plotted against 'x', the mole fraction of phenol. The position, at which the maxima in these curves occur, is related to the number of phenol units (n) combining with one Fe^{3+} by the expression

$$n = x/1-x.$$

FIG. 1

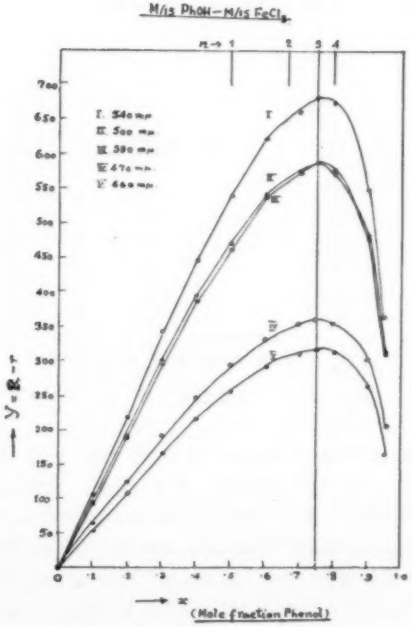
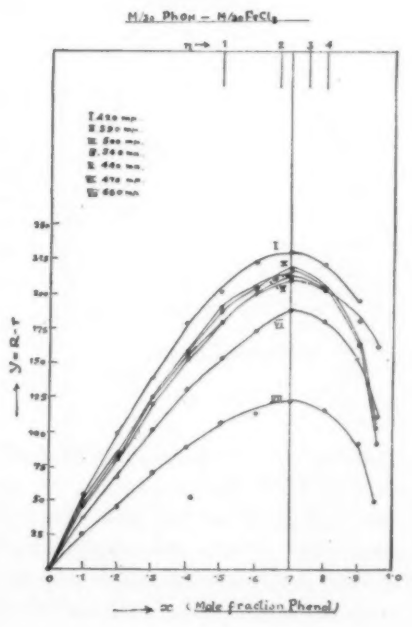


FIG. 2



For the system $M/15$ $FeCl_3 - M/15$ phenol, the maxima in the '$x - Y$' curves lie at $x = 0.75$, *i.e.* $n = 3$ (Fig. 1). The maxima are independent of wave-length. Absorption was measured at 5 different wave-lengths, viz., 470, 500, 540, 590 and 660 mμ. The curves for $M/30$ $FeCl_3 - M/30$ phenol are given in Fig. 2. Measurements were made at 7 different wave-lengths, viz., 420, 440, 470, 500, 540, 590, 660 mμ. The maxima shift to lower values of n. These lie at $x = 0.70$, *i.e.* between $n = 2$ and $n = 3$. On taking a still more dilute system, $M/100$ $FeCl_3 - M/100$ phenol, the curves (Fig. 3) show definite maxima at $x = 0.66$ or $n = 2$. The wave-lengths used for the measurements are: 540, 590 and 660 mμ. It would be possible to show in case of still more dilute systems, the existence of the complex $Fe(OR)_1^{++}$. Due to the fact that the colour produced under these conditions is too faint to be measured accurately, unless very large cells are used, a different method has been used to show the existence of the mono-complex.

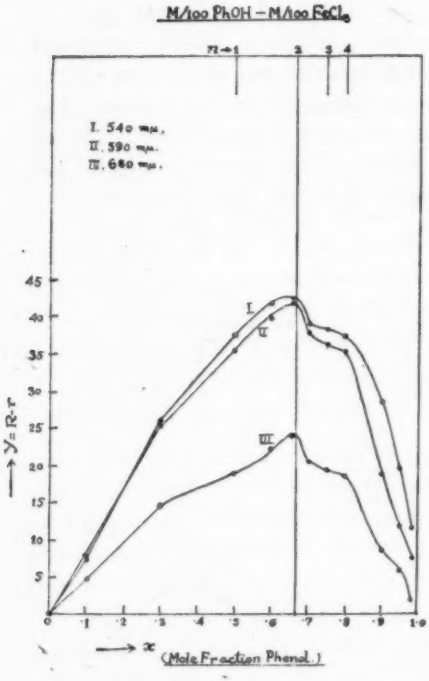


FIG. 3

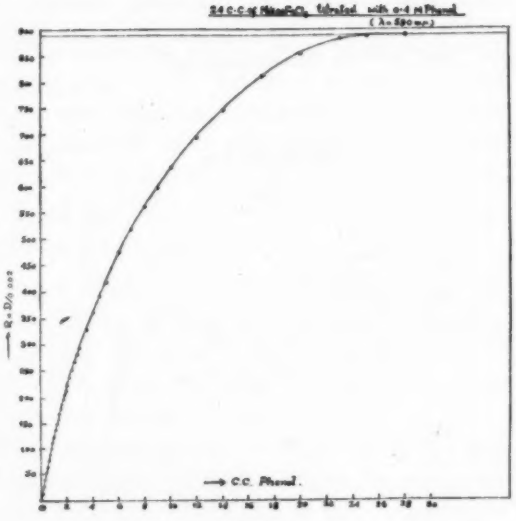


FIG. 4

Colorimetric Titration.—$M/400$-$FeCl_3$ (24c.c.) was taken in a 2 cm. cell and titrated with 0.4M phenol solution. A mechanical glass stirrer was used. Absorption was measured at 590 mμ. This wave-length was chosen because the ferric ion absorption at this wave-length was negligible and that the maximum absorption of the ferric-phenol color was at 558 mμ (Brode, *loc. cit.*). The absorption was recorded after each addition of the reagent (phenol). The readings were

corrected for dilution (assuming Beer's law to hold true) at each stage, because the volume went on changing with the addition of the reagent.

The absorption readings (corrected for dilution), plotted against the amount of phenol added, give a smooth curve (Fig. 4) whose slope gradually falls and tends to zero. The zero slope or colour saturation is approached only when a very large excess of phenol has been added. Actually about 200 moles of phenol to 1 mole of Fe^{3+} was added before the colour saturation took place.

The necessity for so large an amount of the variable constituent is due to the mass effect. The large excess of phenol shifts the equilibrium,

$$\underset{(a-x)}{Fe^{3+}} + \underset{(b-x)}{(OPh)^-} \rightleftharpoons \underset{(x)}{Fe(OPh)^{++}}$$

towards almost complete formation of the complex. The equilibrium constant, K_1, for the reverse reaction is given by $K_1 = (a-x)(b-x)/x$.

The value of K_1 has been calculated and found to remain fairly constant, showing that $Fe(OPh)^{++}$ is the complex that predominates under such conditions.

The saturation value (R), extrapolated to 890 in terms of the reading on the instrument scale is proportional to the concentration (a) of Fe^{3+}, because the whole of Fe^{3+} is converted into the complex at this stage. The concentration (x) of the complex at any moment is proportional to the corresponding reading (r). Thus $x = a.(r/R)$ moles/litre. Values of a, b and x are thus known in terms of moles/litre.

The values of K_1, calculated for this reaction, are tabulated below.

TABLE I

Fe	:	PhOH.	f_{Fe}.	$(K_2 \times 10^4)$.	$(K_1 \times 10^2)$.
1	:	1	0.50	2.5	10.8
1	:	2	0.33	4.9	10.5
1	:	4	0.20	9.7	10.4
1	:	6	0.143	—	10.1
1	:	8	0.110	18.7	10.0
1	:	10	0.091	—	9.9
1	:	12	0.077	—	10.0
1	:	16	0.059	37.8	10.0
1	:	20	0.048	—	10.1
1	:	30	0.032	—	9.9
1	:	40	0.024	82.8	(8.6)

f_{Fe} = mole fraction of Fe^{3+}.

The values of K_1 are fairly constant up to molar ratio 20 : 1 of phenol to Fe^{3+}. The values of equilibrium constants, calculated for higher complexes, e.g. K_2 for $Fe(OPh)_2$ differ very widely from each other, showing that at dilutions such as $M/400$, the mono-complex $Fe(OPh)^{++}$ exists.

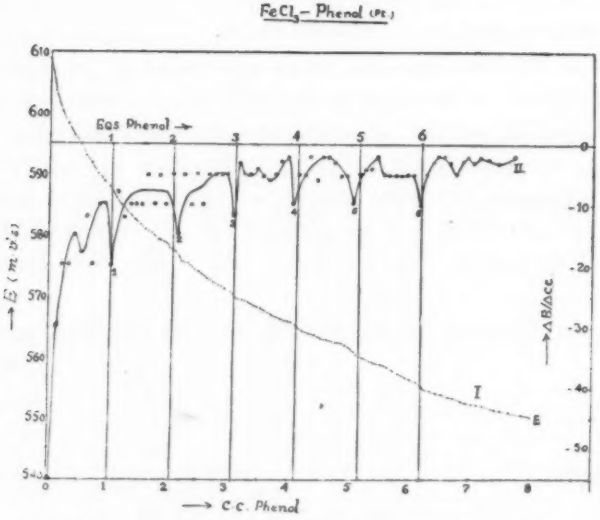
Potentiometric Study.—The oxidation-reduction potential of ferric ion in varying amounts of phenol was measured using the system :

$$Pt^{+}/soln./satd.\ KCl/satd.\ KCl\text{-}Hg_2Cl_2/Hg^{-}.$$

The inflexions in the c. c.—E. M. F. curve, brought out clearly by sharp peaks in the differential graph (mean c. c. vs. $\triangle E/\triangle$c. c.), account for some definite stoichiometric complexes.

7.28 c. c. of 0.092 *M*-$FeCl_3$, diluted to 40 c. c. with distilled water were titrated with 0.67*M*-phenol solution, thorough mixing being effected by means of a magnetic stirrer.

FIG. 5.



The c. c.—E. M. F. graph is represented in Fig. 5 (graph I). Various peaks which occur at regular intervals in the differential curve (graph II, Fig. 5) indicate the following complexes (Table II).

TABLE II

	Position of peaks. Calc.	Obs.	Relative intensity of peaks.		Position of peaks. Calc.	Obs.	Relative intensity of peaks.
$Fe(OPh)_1$	1.02	1.05	20	$Fe(OPh)_4$	4.10	4.05	10
$Fe(OPh)_2$	2.05	2.15	15	$Fe(OPh)_5$	5.12	5.05	10
$Fe(OPh)_3$	3.07	3.05	12	$Fe(OPh)_6$	6.15	6.15	10

Ferric Chloride—m-Cresol

Cresols give blue colour with $FeCl_3$. The colour with *ortho* and *para* isomers is unstable but that of *meta* isomer is stable (Brode, *loc. cit.*).

FIG. 6

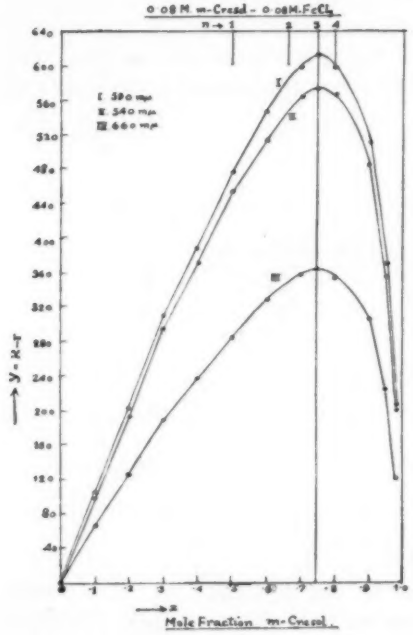
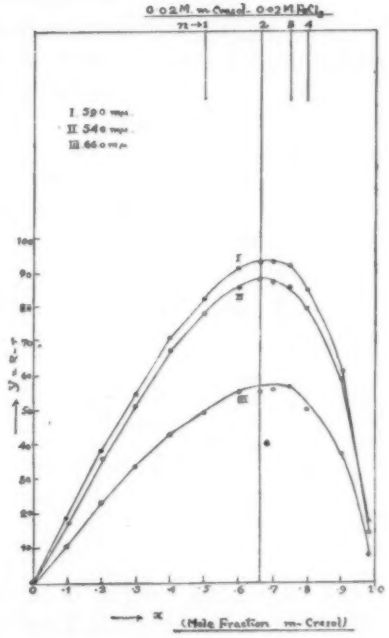


FIG. 7



Job's Continuous Variation.—*m*-Cresol closely resembles phenol in its reaction with $FeCl_3$. The continuous variation of the system $0.08M$-$FeCl_3$—$0.08\ M$ *m*-cresol shows the complex $Fe(OR)_3$. The maxima in the 'x-Y' curves lie at $x=0.75$, or $n=3$, and are independent of wave-length (Fig. 6). Wave-lengths used are : 540, 590 and 660 mμ. The maxima are, however, not independent of concentration of the reactants. The 'x-Y' curves of a dilute system : $0.02M$-$FeCl_3$—$0.02M$ *m*-cresol, show maxima which are shifted to lower values of n (Fig. 7). The curve with $\lambda=540$ mμ shows the maximum at $n=2$, while the curves with $\lambda=590$ mμ and $\lambda=660$ mμ give less definite peaks, but they do lie between $n=2$ and $n=3$, showing thereby that dilution favours lower complexes.

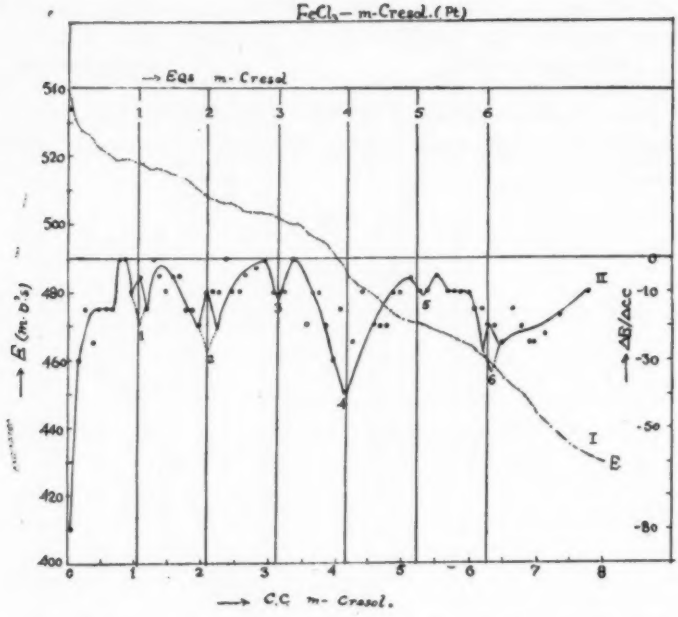
Potentiometric Study.—$M/25$-$FeCl_3$ (5 c. c.) was diluted to 50 c. c. with distilled water and titrated with $M/5$*m*-cresol solution. The system,

$$Pt^{+}/soln./satd.\ KCl/satd.\ KCl\text{-}Hg_2Cl_2/Hg^{-}$$

was used to measure the oxidation-reduction potential of ferric ion in varying amount of *m*-cresol. The titration cell was put in a melting ice-bath in order to

stabilise the colour, which otherwise becomes turbid and fades slowly when kept at room temperature.

FIG. 8



The c.c.—E.M.F. curve is represented in Fig. 8 (graph I). The peaks in the differential curve (graph II, Fig. 8) indicate the following complexes (Table III).

TABLE III

	Position of peaks. Calc.	Obs.	Relative intensity of peaks.
$Fe(OR)_1$	1.04	1.05	20
$Fe(OR)_2$	2.08	2.10	27
$Fe(OR)_3$	3.12	3.15	12
$Fe(OR)_4$	4.15	4.15	40
$Fe(OR)_5$	5.20	5.30	12
$Fe(OR)_6$	6.25	6.30	33

DISCUSSION

A quantitative explanation of the colour of the ferric-phenol complexes has not been attempted so far. Two chromophores are involved in these complexes,

viz. Fe^{3+} ion and the phenolic part, which coupled together produce strong absorption in the visible region of the spectrum. The phenolic chromophores have usually ultraviolet absorption, while the other chromophore, Fe^{3+}, has strong ultraviolet absorption with a comparatively small absorption in the visible.

An attempt has been made to calculate the absorption frequency (ν_c) of the ferric-phenol complex, knowing the individual absorption frequencies (ν_a , ν'_a .....) and (ν_b , ν'_b .....) of the ferric ion and the phenolic part respectively. The colour of the complex has been found to be due to the frequency difference between various absorption frequencies of the constituent chromophores.

FIG. 9 FIG. 10

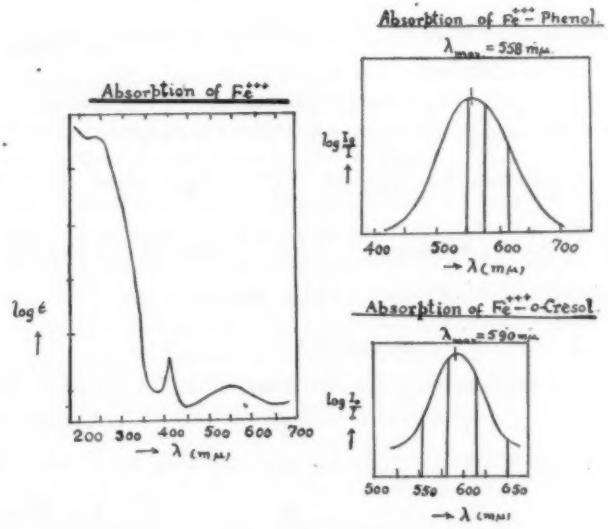


FIG. 11

The ferric ion absorption frequencies, according to Rabinowitch and Stockmeyer (*J. Amer. Chem. Soc.*, 1942, **64**, 335). (Fig. 9) are as shown below.

Frequency.	$Cm^{-1} \times 10^{-3}$.	λ(mμ).	
ν_a	18.5	540	(w)
ν'_a	24.5	407	(s)
ν''_a	$\simeq 52$	$\simeq 194$	(v.s.)

The absorption frequencies of phenol anion, according to Doub and Vandenbelt (*ibid.*, 1947, **69**, 2716) are as shown below.

Frequency.	$Cm^{-1} \times 10^{-3}$.	λ(mμ).	
ν_b	34.8	287	(s)
ν'_b	42.6	235	(v.s.)

From these values, the absorption frequencies of the ferric-phenol complex are calculated.

Frequency.	Calculated (ν_c) $Cm^{-1} \times 10^{-3}$.	$\lambda(m\mu)$.	Observed*	
$\nu_a \sim \nu_b$	16.3	614	(f)	Band width = 425-700 mμ
$\nu''_a \sim \nu_b$	17.2	581	(s)	Absorption max. = 558 mμ
$\nu'_a \sim \nu'_b$	18.1	553	(v.s.)	Brode (*loc. cit.*)
$\nu_a \sim \nu'_b$	24.1	415	(w)	
$\nu''_a \sim \nu'_b$	9.4	1064	Not investigated.	
$\nu'_a \sim \nu_b$	10.3	971		

* (See Fig. 10)

[s. = strong, v.s. = very strong ; f = fair ; w = weak]

A similar calculation for *o*-cresol $-Fe^{3+}$ colour gives the following values for ν_c :—

$\nu_b = 36.6 \times 10^3$ cm^{-1} $(= 274 m\mu)$
$\nu'_b = 35.7 \times 10^3$ cm^{-1} $(= 280 m\mu)$

} Wolf and Herold (*Z. physikal. Chem.*, 1931, B13, 201).

Frequency.	Calculated (ν_c) $Cm^{-1} \times 10^{-3}$.	$\lambda(m\mu)$.	Observed*	
$\nu''_a \sim \nu_b$	15.4	650	w	Band width = 525 - 660 mμ.
$\nu''_a \sim \nu'_b$	16.3	614	s	
$\nu_a \sim \nu'_b$	17.2	581	v.s	Absorption max. = 590 mμ
$\nu_a \sim \nu_b$	18.1	553	s	(Brode, *loc. cit.*)
$\nu'_a \sim \nu'_b$	11.2	893	Not investigated.	
$\nu'_a \sim \nu_b$	12.1	826		

*(See Fig. 11)

It is seen that the absorption of ferric complexes of phenols is made up of a number of frequency differences, (absorption frequency of one chromophore ~ that of the other). The resultant of these is the actual absorption of these compounds in the visible region of the spectrum.

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THE EVALUATION OF TRUE ZETA-POTENTIALS OF QUARTZ PARTICLES OF DIFFERENT SIZE FROM MEASUREMENTS OF STREAMING POTENTIAL

By B. N. Ghosh, S. C. Rakshit and D. K. Chattoraj

It has been pointed out that the "radius effect" of Wood cannot account for the variation of ξ_a with particle size observed by Bull and Gortner.

The equation $\frac{1}{\xi_a} = \frac{1}{\xi} + \frac{m}{r}$, deduced on the basis of surface conductivity correction, connecting ξ_a, the observed zeta-potential with ξ, the true potential and r, the radius of the particles forming the diaphragm, has been subjected to experimental test using the data of Bull and Gortner for quartz particles and has been found to be quite satisfactoty. A plot of $1/\xi_a$ against $1/r$ gave a straight line from the slope and intercept of which m and $1/\xi$ were obtained.

It has recently been shown by Ghosh and Rakshit (*Science & Culture*, 1953, **18**, 498) that the true ξ-potential of the coagulated particles of a titanic oxide sol in contact with solutions of various electrolytes at their equicoagulating concentrations can be evaluated. Bull and Gortner (*J. Phys. Chem.*, 1932, **36**, 111) have investigated the effect of particle size on the electrokinetic potential, using diaphragms of quartz in contact with a solution of $2\times10^{-4}N$-NaCl at 24.5° ± 0.5° by the streaming potential method. Their data indicate that the observed ξ-potential (ξ_a) diminishes as the size of the particles forming the diaphragm decreases.

Ratio of Double layer Thickness to Capillary Diameter and its Effect on ξ_a.— According to Wood (*J. Amer. Chem. Soc.*, 1946, **48**, 433) when the diameter of the pores of the diaphragm decreases and approaches the thickness of the electrical double layer, then the streaming potential and the observed ξ-potential should also decrease. A quantitative relationship has been deduced by Wood (*loc. cit.*) which can be expressed as follows :–

$$\frac{\eta Hk}{P} = M - \frac{1}{2a} \Sigma_i \; d_i \; \Delta M_i \qquad \ldots \qquad \ldots \qquad (1)$$

where η represents viscosity coefficient, and k, the bulk specific conductivity of the solution of electrolyte used, H, the streaming potential corresponding to a pressure P, M, the moment of the electrical double layer, d, its thickness, "a", the radius of the pores of the diaphragms and $\Sigma \Delta M_i = M$.

An approximate calculation of the pore size of the diaphragm made of particles of even the smallest size (*i.e.* 4.6 μ diameter) shows that it is much larger than the thickness of the double layer. Assuming that the packing of the particles in the diaphragm is similar to what occurs when three spheres of diameter 4.6 μ touch one another with their centres lying on the same plane and occupying the corners of an

equilateral triangle of side length $2\times2.3\,\mu$, then the radius of the inner sphere touching the three outer ones is $2.3\left(\frac{2}{\sqrt{3}}-1\right)\mu$. The radius of the pores is therefore of the order of $(2.3\times0.17)\mu$ or 3.9×10^{-5} cm. The thickness of the double layer, when a solid wall is in contact with $10^{-4}N$-NaCl solution, is 3.1×10^{-6} cm. (vide Verwey and Overbeek, "Theory of Stability of Lyophobic Colloids", 1948, p 29), and for the $2\times10^{-4}N$ solution used by Bull and Gortner (*loc. cit.*), it will be still less. Therefore, $\frac{d}{2a}$ is of the order of $\frac{3.1\times10^{-6}}{2\times3.9\times10^{-5}}$ *i. e.* nearly $\frac{3}{80}$. Hence 'd' is small compared to the diameter "$2a$" of the pores. Under the circumstances 'd' can have its full extension and for the given concentration of the NaCl solution it should remain constant. Hence

$$\frac{1}{2a}\Sigma_i\, d_i\, \triangle M_i = \frac{d}{2a}\Sigma_i\, \triangle M_i = \frac{d}{2a}.\, M$$

Wood's equation under the conditions of the experiments of Bull and Gortner can therefore be expressed as

$$\eta H\frac{k}{P} = M\left(1-\frac{d}{2a}\right)$$

$$\text{or}\quad \frac{4\pi\eta Hk}{P.D} = \frac{4\pi M}{D}\left(1-\frac{d}{2a}\right)$$

$$\text{or}\quad \xi_a = \frac{4\pi M}{D}\left(1-\frac{d}{2a}\right) \qquad \ldots \qquad \ldots \qquad \ldots \qquad (2)$$

$$\left[\because\quad \xi_a = \frac{4\pi\eta Hk}{P.D}\right]$$

As $d/2a$ is approximately equal to 3/80 even for the diaphragm made of the smallest particles, the above equation can, at best, account for a 4% variation only of ξ_a with particle size and not five times (approximately) as has actually been observed.

Surface Conductivity of the Capillary Wall and its Effect on ξ_a—The explanation of the variation has therefore to be sought in other directions. It occurred to us that the surface conductance of the capillary wall of the diaphragm might be responsible for the phenomenon observed. According to Bikerman (*Trans. Faraday Soc.*, 1940, 35, 154) and Rutgers (*ibid.*, 1940, 35, 69) the conductivity of the solution per unit volume inside the capillaries of the diaphragm is equal to $\left(k+\frac{2\lambda}{r}\right)$, where k represents the bulk specific conductivity, λ, the specific surface conductivity of the wall of the capillary of radius 'r'. Therefore, the true zeta-potential

$$\xi = \frac{4\pi\eta H\left(k+\frac{2\lambda}{r}\right)}{P.D}$$

$$\text{or,}\quad \xi = \frac{4\pi\eta Hk}{P.D}\left(1+\frac{2\lambda}{kr}\right)$$

$$= \xi_a\left(1+\frac{2\lambda}{kr}\right)$$

$$\therefore\quad \xi/\xi_a = 1+2\lambda/kr$$

Putting $2\lambda/k = m'$ and rearranging, we have,

$$\frac{1}{\xi_a} = \frac{1}{\xi} + \frac{m'}{\xi} \cdot \frac{1}{r}.$$

So long as the quartz particles are in contact with the NaCl solution of the same concentration, ξ remains constant. Hence, m'/ξ may be put equal to m, a constant.

We therefore have,

$$\frac{1}{\xi_a} = \frac{1}{\xi} + \frac{m}{r} \qquad \ldots \qquad \ldots \qquad (3)$$

It may be mentioned here, that the application of equation (3) is based on two assumptions which are the same as those made by Wood in applying his equation (1) to the experimental data of Bull and Gortner (*loc. cit.*). The assumptions are that (*i*) the diaphragm may be treated as equivalent to a uniform capillary tube of proper dimensions and (*ii*) the radius of the pores is a linear function of the radius of the quartz particles of which the diaphragm is made.

Recently some doubt has been cast on the validity of the assumption (*i*). Overbeek and Wijga (*Rec. trav. chim.*, 1946, **65**, 556) have suggested that a diaphragm should be treated as equivalent to a number of capillaries of different diameters connected in series with each other. Taking the case of two capillaries of different diameters connected in series, they have shown that the true ξ is given by the relation

$$\frac{H}{P} = \frac{D\xi}{4\pi\eta} \cdot \left(\frac{c_1 w_1 R_1 + c_2 w_2 R_2}{w_1 + w_2} \right)$$

In the above equation, H, P, D and ξ have the same significance as before, while

$$c_1 = \frac{\pi r_1^2}{l_1}, \quad c_2 = \frac{\pi r_2^2}{l_2}, \quad R_1 = \frac{l_1}{\pi r_1^2 \left(k + \frac{2\lambda}{r_1} \right)}$$

$$R_2 = \frac{l_2}{\pi r_2^2 \left(k + \frac{2\lambda}{r_2} \right)}, \quad w_1 = \frac{8\eta l_1}{\pi r_1^4} \text{ and } w_2 = \frac{8\eta l_2}{\pi r_2^4}.$$

Here r_1, r_2 and l_1, l_2 represent the radii and lengths respectively of the two capillaries, and k and λ have the same significance as before,

$$\xi = \frac{4\pi\eta H}{DP} \left(\frac{w_1 + w_2}{c_1 w_1 R_1 + c_2 w_2 R_2} \right)$$

$$= \frac{4\pi\eta}{D} \cdot \frac{Hk}{P} \left\{ \frac{w_1 + w_2}{\frac{w_1}{1 + \frac{2\lambda}{kr_1}} + \frac{w_2}{1 + \frac{2\lambda}{kr_2}}} \right\}$$

$$\text{or,} \qquad \xi = \xi_a \left\{ \frac{\left(1 + \frac{2\lambda}{kr_1} \right)\left(1 + \frac{2\lambda}{kr_2} \right)}{1 + \frac{2\lambda}{k} \left\{ \frac{w_1 r_1 + w_2 r_2}{r_1 r_2 (w_1 + w_2)} \right\}} \right\} \qquad (5)$$

Let us suppose $r_1 > r_2$, so that $r_2 = ar_1$, where 'a' is a fraction much less than unity. If we consider the application of the above equation to an actual diaphragm made of fine particles, then it becomes evident that the walls of a capillary having a larger radius, have a much greater chance of collapsing than that of a capillary having a smaller radius. Therefore, the length of a stable capillary having a larger radius will in all probability be less than that of a capillary having a smaller radius *i.e.*, l_1 will be less than l_2.

Now, substituting ar_1 for r_2 in equation (5), we have

$$\xi = \xi_a \left\{ \frac{\left(1+\frac{2\lambda}{kr_1}\right)\left(1+\frac{2\lambda}{kar_1}\right)}{1+\frac{2\lambda r_1}{kar_1^2}\left(\frac{l_1}{r_1^4}+\frac{l_2 a}{a^4 r_1^4}\right)\Big/\left(\frac{l_1}{r_1^4}+\frac{l_2}{a^4 r_1^4}\right)} \right\}$$

$$\text{or} \quad \frac{\xi}{\xi_a} = \frac{\left(1+\frac{2\lambda}{kr_1}\right)\left(1+\frac{2\lambda}{kar_1}\right)}{1+\frac{2\lambda}{kar_1}\left(\frac{l_1 a^4}{l_2}+a\right)\Big/\left(\frac{l_1 a^4}{l_2}+1\right)} \qquad \ldots \qquad (6)$$

Since $a<1$ and if l_1 is less than or even equal to l_2 then terms involving a^4 can be neglected without introducing much error. Equation (6) thus reduces to the form

$$\frac{\xi}{\xi_a} = \frac{\left(1+\frac{2\lambda}{kr_1}\right)\left(1+\frac{2\lambda}{kar_1}\right)}{\left(1+\frac{2\lambda a}{kr_1 a}\right)}$$

$$\text{or} \quad \frac{\xi}{\xi_a} = 1+\frac{2\lambda}{kar_1} = 1+\frac{2\lambda}{kr_2} \qquad \ldots \qquad (7)$$

Since $ar_1 = r_2$, it is evident from equation (7) that the capillary with the smallest diameter regulates ξ_a. Now so long as the material of the capillary tubes or the diaphragm is the same, and the concentration of the given electrolyte is the same, λ and k remain constant. Therefore, equation (3), which is of the same form as equation (7), can be applied to the experimental data of Bull and Gortner (*loc. cit.*). Their experimental data are recorded in Table I. In calculating Hk/P they used 2.89×10^{-5} mhos as the value of k in every case, except for the diaphragm made of the particle size 4.6μ. In Table I, however, the same value of bulk specific conductivity k viz., 2.89×10^{-5} mhos has been used throughout, no exception being made for the diaphragm of the smallest particle size. The values of ξ_a recorded in column 4 of Table I have been obtained from the well known relation* (vide Table II).

$$\xi_a = \frac{4\pi\eta k}{D}\cdot\frac{H}{P},$$

where $\eta = 0.009$ poise, is the viscosity and $D = 78$, the dielectric constant of water at 25°. In the last column are recorded the values of ξ_a calculated from equation (3) for different values of r, the radius of the quartz particles.

TABLE I

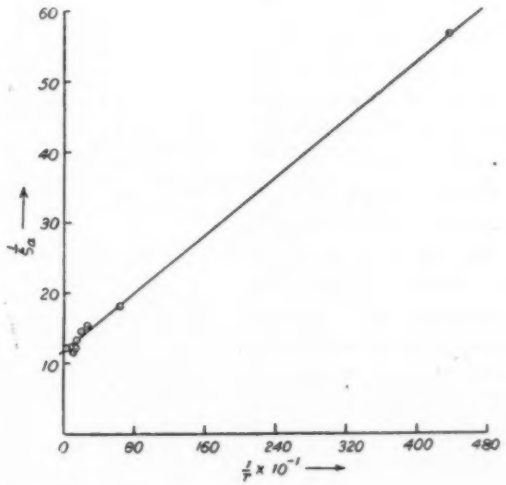
$k_s = 2.89 \times 10^{-5}$ mhos.

Diameter.	Reciprocal of radius $\left(\frac{1}{r} \times 10^4\right)$.	H/P (mv/cm. of Hg).	Observed ξ_a.	Calculated ξ_a from equation (3).
630 μ	0.003174	29.04	0.0821 volt	0.0831 volt
330	0.00606	29.10	0.08226	0.0811
214	0.009346	30.15	0.08523	0.0790
163	0.01227	29.31	0.08285	0.0771
128	0.01563	26.62	0.07525	0.07513
98	0.0204	24.19	0.06837	0.0724
74.9	0.0267	22.93	0.06482	0.0691
31.1	0.0643	20.12	0.05687	0.0545
4.59	0.4358	6.25	0.01767	0.01763

* $\xi = \frac{Hk}{P} \cdot \frac{9 \times 10^{11} \times 4 \times 3.142 \times 0.009 \times 300}{13.6 \times 981 \times 10^3 \times 78 \times 300}$ where ξ_a is expressed in volts, H in millivolts, k in mhos. and P in centimeters of mercury.

It will be noticed from the data recorded in the above table that the

FIG. 1



agreement between the observed values of ξ_a and those calculated from equation (3), taking $1/\xi = 11.7$ and $m = 0.01033$, is quite satisfactory, specially in view of the

probable limits of error in these experiments. It will be noticed from Fig. 1 that a plot of the reciprocal of observed ξ_a against the reciprocal of the radius r, gives a straight line. From the slope and intercept of this line with the $\frac{1}{\xi_a}$ axis, "m" and $1/\xi$ stated above were obtained. The value of ξ from $1/\xi$ can be easily calculated and this gives the true zeta-potential of the quartz particles in contact with $2\times10^{-4}N$-NaCl solution. It is independent of the size of the particles and is found to be 0.085 volts.

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FERRIC COMPLEXES OF PHENOLS. PART II. SALICYL ALDEHYDE AND *o*-HYDROXYACETOPHENONE

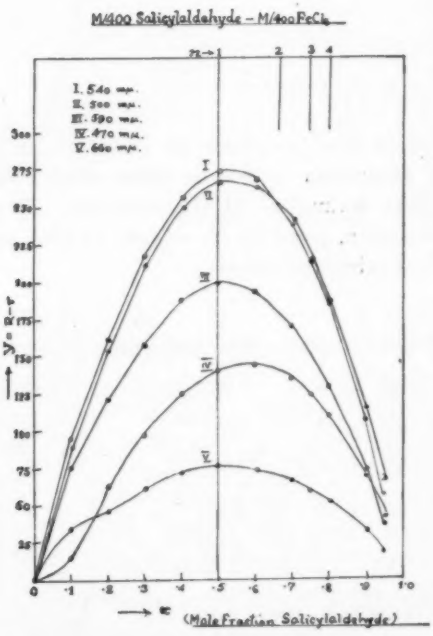
By S. K. K. Jatkar and B. N. Mattoo

The ferric complexes of salicylaldehyde and *o*-hydroxyacetophenone have been studied in aqueous solution at low concentration by Job's method of continuous variation and by colorimetric titrations. The curves of continuous variation show maxima at 1 : 1 ratio. The agreement in the values of equilibrium constants calculated for the reactions, on the assumption of a mono-complex, confirms the existence of mono-complex.

Salicylaldehyde gives a stable purple-red colour with $FeCl_3$, the absorption maximum of this colour being at 533mμ (Brode, *J. Amer. Chem. Soc.*, 1934, 56 1037). The ferric-salicylaldehyde complex has been studied, in the present work colorimetrically by Job's continuous variation method and a colorimetric titration. Evidence for ferric mono-salicylaldehyde complex in aqueous solution has been obtained.

Job's Continuous Variation.—Equimolar solutions (*M*/400) of salicylaldehyde and $FeCl_3$ were mixed in varying proportion. The absorption of the resulting solutions was measured on a Klett-Sommerson photoelectric colorimeter. The difference '*Y*' between the absorption observed for a solution minus the absorption calculated for no reaction, plotted against '*x*', the mole fraction of salicylaldehyde, gives a curve with maxima at $x = 0.5$ or $n = 1$. The maxima are independent of wave-length. Measurements were made at 470, 500, 540, 590, and 660mμ. (Fig. 1).

FIG. 1.



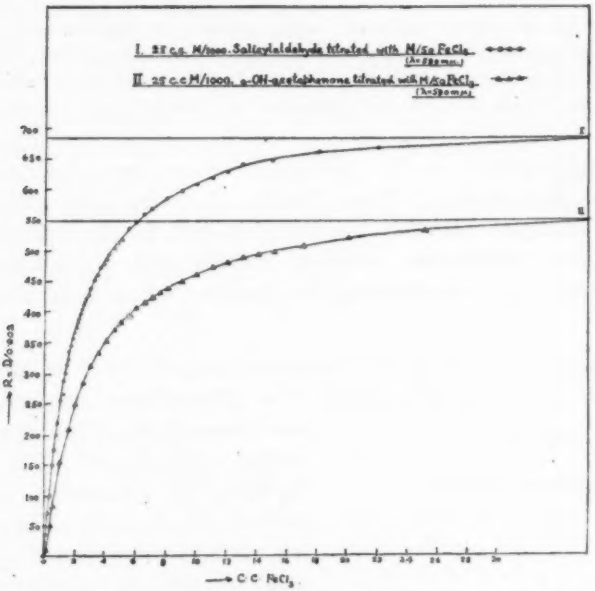
Colorimetric Titration.—*M*/1000 aqueous salicylaldehyde solution (25 c. c.) was taken in a 2 cm. cell and titrated with *M*/50-$FeCl_3$, which was added from a burette. The reaction was followed by the measurement of absorption at 590mμ, Fe^{3+} absorption at this wave-length being negligible as compared to that of the complex. Absorption readings were taken after each addition of the reagent (Fe^{3+}). Readings, corrected for dilution at each stage, when plotted against the amount of Fe^{3+} added, give a smooth curve whose slope gradually falls and tends to zero (Fig. 2). From the saturation value of absorption,

extrapolated to a reading of 685 on the scale of the instrument, the values of 'x' in the equilibrium,

$$\underset{(b-x)}{Fe^{3+}} + \underset{(a-x)}{(OR)'} \rightleftharpoons \underset{(x)}{Fe(OR)^{2+}} \quad \ldots \quad \ldots \quad \text{'}i\text{'}$$

are evaluated in terms of moles/litre (described in Part I, this *issue*, p. 592).

FIG. 2


I. 25 c.c. M/1000 Salicylaldehyde titrated with M/60 FeCl3
II. 25 c.c M/1000 o-OH-acetophenone titrated with M/60 FeCl3
R. D/cms
c.c FeCl3

The large excess of the variable component (Fe^{3+}), about 16 moles to one mole of salicylaldehyde, for producing colour saturation is due to mass effect; it shifts the equilibrium towards almost complete formation of the complex. The equilibrium constant 'K_1' for the reverse reaction, given by $K_1 = (a\text{-}x)\ (b\text{-}x)/x$, is calculated for the reaction and various values are tabulated below.

TABLE I

Fe^{3+} : Sal.	f_{Fe}.	$K_2 \times 10^9$.	$(K_1 \times 10^4)$.	Fe^{3+} : Sal.	f_{Fe}.	$K_2 \times 10^9$.	$(K_1 \times 10^4)$.
1.0 : 4	0.20	311	(6)	4.0 : 1	0.80	...	10
1.0 : 2	0.33	199	(7)	5.0 : 1	0.83	...	10
1.0 : 1	0.50	27	8	6.0 : 1	0.857	...	10
1.2 : 1	0.54	4	8	8.0 : 1	0.88	...	9
2.0 : 1	0.66	...	9	12.0 : 1	0.923	...	(6)
3.0 : 1	0.75	...	10				

(f_{Fe} = mole fraction of Fe^{3+})

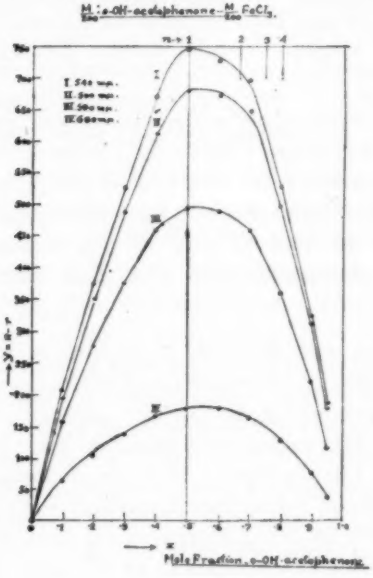
Values of 'K_1' remain fairly constant between mole fraction 0.50 and 0.88 of ferric On either side of this range, the values are no longer constant. It is only with

the assumption of a mono-complex that the values are somewhat constant ; however, with the assumption of higher complexes, equilibrium constants are widely apart from each other, e.g., K_2 for disalicylaldehyde complex.

o-Hydroxyacetophenone resembles closely salicylaldehyde in its reaction with $FeCl_3$. It gives a similar stable purple-red colour. Job's continuous variation method and a colorimetric titration show the existence of the mono-complex. No metallic complexes of *o*-hydroxyacetophenone have been reported.

Job's Continuous Variation.—*M*/200 solutions of *o*-hydroxyacetophenone and $FeCl_3$ were mixed in varying proportion. Absorption was measured at 500, 540, 590, 660 mμ. The '*x*-*Y*' curves show the maxima at $x=0.5$ or $n=1$, the maxima being independent of wave-length (Fig. 3).

FIG. 3



Colorimetric Titration.—*M*/1000-*o*-hydroxyacetophenone solution (25 c. c.) was titrated with *M*/50-$FeCl_3$ in a 2 cm. cell. The absorption readings (corrected for dilution) plotted against the amount of Fe^{3+} added, give a smooth curve, whose slope falls gradually and tends to zero (Fig. 2). The saturation value of the colour extrapolated to a reading of 550 on the scale of the instrument, enables us to evaluate the values of '*x*' in the equilibrium (*i*), in terms of moles/litre.

The values of $K_1=(a-x)(b-x)/x$, are calculated and found to remain fairly constant up to mole fraction 0.9 of Fe^{3+}. The agreement in these values is better than those calculated for salicylaldehyde-Fe^{3+} complex. The values of K_1 are given below.

TABLE II

Fe^{3+} : R-OH.	f_{Fe}.	$K_2\times10^8$.	$(K_1\times10^4)$.	Fe^{3+} : R-OH.	f_{Fe}.	$K_2\times10^8$.	$(K_1\times10^4)$.
0.25 : 1	0.20	...	15	2.00 : 1	0.66	...	14
0.40 : 1	0.286	81.4	14	3.00 : 1	0.75	...	14
0.50 : 1	0.33̇	...	14	4.00 : 1	0.80	...	14
0.80 : 1	0.44̇	34.1	13	5.00 : 1	0.83̇	...	14
1.00 : 1	0.50	22.8	14	6.00 : 1	0.857	...	14
1.20 : 1	0.54̇	12.5	13	8.00 : 1	0.88̇	...	13
1.60 : 1	0.615	2.0	14	10.00 : 1	0.91	...	(12)

(f_{Fe}=mole fraction of Fe^{+3} ; R-OH=*o*-hydroxyacetophenone).

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BROMINATION OF COUMARINS. PART III. BROMINATION OF SOME 5-HYDROXYCOUMARIN DERIVATIVES AND THEIR METHYL ETHERS

By S. S. Lele, R. J. Parikh and Suresh Sethna

5-Hydroxy-4-methyl- and 5-hydroxy-4 : 7-dimethyl-coumarin and their methyl ethers have been brominated with one mole, two moles and with excess of bromine. The first bromine atom is found to enter the 8-position in all cases. Ths second bromine atom has been found to enter the 6-position in the case of the hydroxycoumarins and the 3-position in the case of the methoxycoumarins. With excess of bromine the 3 : 6 : 8-tribromocoumarins have been obtained.

In the bromination of 7-hydroxy- and 6-hydroxycoumarin derivatives the first bromine atom has been found to enter the 3-position (Dalvi and Sethna, this *Journal*, 1949, **26**, 359, 467). It has, however, been found by Dey and Kutti (*Proc. Nat. Inst. Sci. India*, 1940, **6**, 641) that in the bromination of 8-methoxycoumarin the first bromine atom enters the 5-position. In view of this it was thought of interest to study the bromination of 5-hydroxycoumarins and their methyl ethers.

5-Hydroxy-4-methylcoumarin on bromination with one mole of bromine gave a product the methyl ether of which did not give a coumarilic acid derivative on heating with alkali, indicating that the first bromine atom had not entered the 3-position. The methyl ether was subjected to Elbs persulphate oxidation when the oxidation product was obtained in good yield. This indicated that the 6-position must be free, for the Elbs persulphate oxidation of 6-substituted coumarins is very difficult (Dalvi, Desai and Sethna, this *Journal*, 1951, **28**, 366). Moreover, the oxidation product gives an orange-yellow colour with alkali which appears to be characteristic of the bromo derivatives of 6-hydroxycoumarins (Dalvi and Sethna, *loc. cit.*). The monobromo product has therefore been assigned the structure of 5-hydroxy-8-bromo-4-methylcoumarin. 5-Methoxy-4-methylcoumarin gave on bromination with one mole of bromine the same monobromo product as the methyl ether of the 5-hydroxy-8-bromo-4-methylcoumarin.

An attempt was made to seek further confirmation of this structure by the synthesis of 5-hydroxy-8-bromo-4-methylcoumarin by another method. Methyl 5-hydroxy-4-methylcoumarin-6-carboxylate was brominated with one mole of bromine when a monobromo product was obtained, the methyl ether of which did not give a coumarilic acid, thus indicating that the bromine had entered the 8-position. The bromo-ester was hydrolysed to the corresponding acid. Attempts to decarboxylate the acid in a sealed tube, and by the quinoline-copper powder method, however, failed to give the required bromocoumarin, the bromine being knocked off during the decarboxylation.

5-Hydroxy-4-methylcoumarin on bromination with two moles of bromine gave a dibromo product, the methyl ether of which did not give a coumarilic acid on heating with alkali. It is therefore assigned the structure of 5-hydroxy-6 : 8-dibromo-4-methylcoumarin. 5-Methoxy-4-methylcoumarin on bromination with two moles of bromine did not give a pure product but with 4 moles of bromine a dibromo product was obtained which gave a bromocoumarilic acid and was found to be different from the methyl ether of 5-hydroxy-6 : 8-dibromo-4-methylcoumarin. Hence, the structure of 5-methoxy-3 : 8-dibromo-4-methylcoumarin is assigned to this product.

The bromination of 5-hydroxy-4-methylcoumarin with excess of liquid bromine gave a tribromo derivative, the methyl ether of which was identical with the tribromo derivative obtained from 5-methoxy-4-methylcoumarin. This product gave a coumarilic acid derivative. The 3 : 6 : 8-tribromo structures have therefore been assigned to these products. The hydroxy-tribromo compound gave a black, very high melting product, immediately, on heating with alcohol or acetone.

The bromination of 5-hydroxy-4 : 7-dimethylcoumarin and its methyl ether was carried out to see whether it followed the same pattern. The results were found to be similar. The monobromo product obtained by the bromination of the hydroxycoumarin was methylated and was found to be identical with the monobromo product of the methyl ether. The methylated product did not give any coumarilic acid on boiling with alkali. It gave on Elbs persulphate oxidation, the oxidation product in good yield, thus indicating that the first bromine atom had entered the 8-position. Further, the hydroxy-monobromo product has a m. p. of 257-58° and is distinctly different from the product of m. p. 217° obtained on Pechmann condensation of 4-bromo-orcinol with ethyl acetoacetate which has been assigned the structure of 5-hydroxy-6-bromo-4 : 7-dimethylcoumarin (Chakravarti and Mazumdar, this *Journal*, 1937, **14**, 725). It may be mentioned here that Desai and Gaitonde (*Proc. Ind. Acad. Sci.*, 1947, **25A**, 366) have arbitrarily assigned the structure of 5-hydroxy-3-bromo-4 : 7-dimethylcoumarin to the compound obtained on bromination of 5-hydroxy-4 : 7-dimethylcoumarin. They used more than 1.5 moles of bromine. On careful repetition of the work under their conditions the substance of m.p. 217°, as stated by them, could not be obtained.

The hydroxycoumarin on bromination with two moles of bromine gave a product to which the structure of 5-hydroxy-6 : 8-dibromo-4 : 7-dimethylcoumarin has been assigned as its methyl ether did not give any coumarilic acid. 5-Methoxy-4 : 7-dimethylcoumarin on bromination with two moles of bromine gave a product which gave a bromocoumarilic acid and was found to be different from the above methyl ether. Hence, the structure of 5-methoxy-3 : 8-dibromo-4 : 7-dimethylcoumarin has been assigned to this product.

With excess of liquid bromine both the hydroxy and the methylated coumarins gave the tribromo derivatives to which 3 : 6 : 8-tribromocoumarin structures have been assigned.

EXPERIMENTAL

5-Hydroxy-4-methylcoumarin-6-carboxylic acid and its methyl ester and 5-hydroxy-4-methylcoumarin and its methyl ether were prepared according to the method of Sethna, Shah and Shah (*J. Chem. Soc.*, 1938, 228).

Bromination of 5-Hydroxy-4-methylcoumarin and its Methyl Ether

(*i*) *Bromination with one mole of Bromine* : *5-Hydroxy-8-bromo-4-methylcoumarin.*—5-Hydroxy-4-methylcoumarin (0.5 g.) was dissolved in hot acetic acid (10.0 c.c.) and the solution while hot was treated with bromine (0.45 g.) in acetic acid (4.5 c.c.). After an hour a brown crystalline mass separated which crystallised from dilute acetic acid in needles (0.2 g.), m.p. 256°. (Found : Br, 30.7. $C_{10}H_7O_3Br$ requires Br, 31.4 per cent).

The *methyl ether* was prepared by dissolving the above product (0.3 g.) in acetone (20 c.c.) and refluxing with dimethyl sulphate (0.25 g.) and anhydrous potassium carbonate (1 g.) for 20 hours. The potassium carbonate was filtered and acetone evaporated. The residue obtained was crystallised from dilute alcohol, m.p. 223° (Found : Br, 29.7. $C_{11}H_9O_3Br$ requires Br, 29.7 per cent).

The same product was obtained when 5-methoxy-4-methylcoumarin (0.5 g.) in acetic acid (10 c.c.) was treated with bromine (0.4 g.) in acetic acid (4 c.c.). The methoxybromocoumarin (0.3 g.) was refluxed with sodium hydroxide (10%, 20 c.c.) for 2 hours. The resulting solution on acidification gave back the starting material.

Elbs Persulphate Oxidation of 5-Methoxy-8-bromo-4-methylcoumarin : 5-Methoxy-6-hydroxy-8-bromo-4-methylcoumarin.—The methoxybromocoumarin (1 g.) was dissolved in sodium hydroxide solution (40 c.c., 10%) by warming on a steam-bath. The solution was then cooled and potassium persulphate (1.1 g. in 25 c.c. of water) was added gradually from a separating funnel during 2 hours. The solution was mechanically stirred and the temperature was not allowed to rise above 10°. The reaction mixture was then kept overnight. The next day it was just acidified with concentrated hydrochloric acid when the original substance (0.3 g.) was obtained. This was filtered and the filtrate was extracted with ether and the aqueous layer was heated on a boiling water-bath with concentrated hydrochloric acid (25 c.c.) for 40 minutes. The product which separated on cooling crystallised from rectified spirit in needles (0.3 g.), m.p. 230°. It dissolves in alkali with an orange colour. (Found : C, 45.6 ; H, 3.6. $C_{11}H_9O_4Br$ requires C, 46.3 ; H, 3.2 per cent).

(*ii*) *Bromination with two moles of Bromine* : *5-Hydroxy-6 : 8-dibromo-4-methylcoumarin.*—5-Hydroxy-4-methylcoumarin (0.3 g.) in acetic acid (10 c.c.) was treated with bromine (0.5 g.) in acetic acid (5 c.c.) in hot. The product which separated

on cooling crystallised from dilute alcohol in needles (0.25 g.), m.p. 227°. (Found : Br, 47.5. $C_{10}H_6O_3Br_2$ requires Br, 47.9 per cent).

The *methyl ether*, prepared by the dimethyl sulphate-acetone-potassium carbonate method as usual, crystallised from dilute acetic acid in needles, m.p. 214-15°. (Found : Br, 45.9. $C_{11}H_8O_3Br_2$ requires Br, 46.0 per cent).

5-Methoxy-6 : 8-dibromo-4-methylcoumarin (0.5 g.) was refluxed with NaOH (10%, 20 c.c.) for 2 hours. The resulting solution on acidification gave the original methyl ether.

5-*Methoxy*-3 : 8-*dibromo*-4-*methylcoumarin*.—5-Methoxy-4-methylcoumarin (0.5 g.) in acetic acid (15 c.c.) was treated with bromine (1.6 g., 4 moles) in acetic acid (16 c.c.). The reaction mixture was then heated on a steam-bath for 2 hours. The product obtained on dilution was crystallised from dilute acetic acid in yellow needles (0.6 g.), m.p. 168°. (Found : Br, 45.9. $C_{11}H_8O_3Br_2$ requires Br, 46.0 per cent).

4-*Methoxy*-7-*bromo*-3-*methylcoumarilic Acid*.—The above dibromocoumarin (0.5 g.) was refluxed with NaOH solution (10%, 20 c.c.) for 2 hours. The product obtained on acidification was crystallised from acetic acid in needles (0.2 g.), m.p. 270°. It gave a green colour with hot concentrated sulphuric acid. (Found : C, 46.9 ; H, 3.6. $C_{11}H_9O_4Br$ requires C, 46.3 ; H, 3.2 per cent).

(*iii*) *Bromination with excess of Liquid Bromine* : 5-*Hydroxy*-3 : 6 : 8-*tribromo*-4-*methylcoumarin*.—5-Hydroxy-4-methylcoumarin (0.3 g.) in acetic acid (20 c.c.) was treated with excess of liquid bromine (2 g.). The reaction mixture was then refluxed on a steam-bath for 1 hour. The product separating on cooling crystallised from acetic acid in yellow needles (0.5 g.), m.p. 238°. (Found : Br, 58.8. $C_{10}H_5O_3Br_3$ requires Br, 58.1 per cent). On boiling with alcohol and acetone the tribromo derivative gave a black product. On extracting this with acetic acid a dark brown product was obtained which did not melt till 290° but left no residue on heating on a spatula. This product has not been worked up further.

The *methyl ether* was prepared by dissolving the above product (0.3 g.) in benzene (70 c.c.) and refluxing with anhydrous potassium carbonate and dimethyl sulphate (0.3 g.) for 20 hours. The product, obtained on working up as usual, crystallised from acetic acid in shining needles (0.2 g.), m.p. 183-84°. (Found : Br, 55.8. $C_{11}H_7O_3Br_3$ requires Br, 55.2 per cent).

The same product was obtained when 5-methoxy-4-methylcoumarin (0.5 g.) in acetic acid (20 c.c.) was treated with bromine (3 g.) in acetic acid (30 c.c.).

4-*Methoxy*-5 : 7-*dibromo*-3-*methylcoumarilic Acid*.—5-Methoxy-3 : 6 : 8-tribromo-4-methylcoumarin (0.5 g.) was refluxed with NaOH (10%, 20 c.c.) for 2 hours. The solid obtained on acidification was crystallised from acetic acid in needles (0.2 g.), m.p. 286°. (Found : C, 36.4 ; H, 2.2. $C_{11}H_8O_4Br_2$ requires C, 36.3 ; H, 2.2 per cent). The acid gave a greenish coloration with hot concentrated sulphuric acid.

Bromination of Methyl 5-Hydroxy-4-methylcoumarin-6-carboxylate and its Methyl Ether with one mole of Bromine

Methyl 5-Hydroxy-8-bromo-4-methylcoumarin-6-carboxylate.—The coumarin ester (0.4 g.) was dissolved in hot acetic acid (10 c.c.) and the solution while hot was treated with bromine (0.27 g.) in acetic acid (2.7 c.c.). The product which separated on cooling crystallised from dilute alcohol in yellow needles (0.3 g.), m.p. 214°. (Found : Br, 25.2. $C_{12}H_9O_5Br$ requires Br, 25.6 per cent).

5-Hydroxy-8-bromo-4-methylcoumarin-6-carboxylic Acid.—The coumarin acid (0.5 g.) was dissolved in hot acetic acid (15 c.c.) and the solution while hot was treated with bromine (0.36 g.) in acetic acid (3.6 c.c.). The product separating on cooling was crystallised from acetic acid in needles, m.p. 266°. (Found : Br, 26.3. $C_{11}H_7O_5Br$ requires Br, 26.8 per cent).

The same acid was obtained by hydrolysing the ester described above by keeping in contact with cold sodium hydroxide (10%, 20 c.c.) for 48 hours.

The *methyl ether* of methyl 5-hydroxy-8-bromo-4-methylcoumarin-6-carboxylate was prepared by dissolving the compound (0.5 g.) in acetone (20 c.c.) and refluxing with methyl iodide (1 c.c.) and anhydrous potassium carbonate (1 g.) for 20 hours. A pasty mass was obtained on working up as usual. This was washed with petroleum ether and crystallised from alcohol in needles, m.p. 100-102°. (Found : Br, 24.2. $C_{13}H_{11}O_5Br$ requires Br, 24.5 per cent).

5-Methoxy-8-bromo-4-methylcoumarin-6-carboxylic Acid.—Methyl 5-hydroxy-8-bromo-4-methylcoumarin-6-carboxylate (0.5 g.) was refluxed with NaOH (10%, 20 c.c.) for 2 hours. The product obtained on acidification was crystallised from alcohol in needles, m.p. 144°. (Found : Br, 25.1. $C_{12}H_9O_5Br$ requires Br, 25.6 per cent).

Bromination of 5-Hydroxy-4 : 7-dimethylcoumarin and its Methyl Ether.

5-Hydroxy-4 : 7-dimethylcoumarin was prepared according to Pechmann and Cohen (*Ber.*, 1884, **17**, 2187), and was methylated in acetone solution with methyl iodide as usual, m.p. 147°. Collie and Crystall (*J. Chem. Soc.*, 1907, **91**, 1805) give m.p. 146°.

(*i*) *Bromination with one mole of Bromine : 5-Hydroxy-8-bromo-4 : 7-dimethylcoumarin.*—5-Hydroxy-4 : 7-dimethylcoumarin (1.9 g.) in acetic acid (40 c.c.) was treated with bromine (1.6 g.) in acetic acid (16 c.c.) in hot. The product separating on cooling was crystallised from acetic acid in shining needles (1.g), m.p. 257-58° (decomp.). (Found : Br, 29.3. $C_{11}H_9O_3Br$ requires Br, 29.7 per cent). It formed a yellow salt with alkali.

5-Methoxy-8-bromo-4 : 7-dimethylcoumarin.—The monobromo product (0.5 g.) was dissolved in acetone (50 c.c.) and refluxed with dimethyl sulphate (1 c.c.) and anhydrous K_2CO_3 (1 g.) for 20 hours. The product obtained on working up as usual was crystallised from acetic acid in tiny needles (0.5 g.), m.p. 190°. (Found : Br, 28.6. $C_{12}H_{11}O_3Br$ requires Br, 28.3 per cent).

The same product was obtained when 5-methoxy-4 : 7-dimethylcoumarin (2 g.) in hot acetic acid (20 c.c.) was treated with bromine (1.6 g.) in acetic acid (16 c.c.).

The methyoxybromocoumarin (0.5 g.) was refluxed with sodium hydroxide (10% ; 10 c.c.) for 4 hours. The resulting solution on acidification gave the starting material.

Elbs Persulphate Oxidation of 5-*Methoxy*-8-*bromo*-4 : 7-*dimethylcoumarin* : 5-*Methoxy*-6-*hydroxy*-8-*bromo*-4 : 7-*dimethylcoumarin.*—The methoxybromocoumarin (1 g.) was dissolved NaOH (3 g. in 30 c.c. water) by warming on a steam-bath. The solution was then cooled and oxidised with potassium persulphate (1.1 g. in 25 c.c. water) during 2 hours. On working up as usual 6-hydroxy-5-methoxy-8-bromo-4 : 7-dimethylcoumarin was obtained. It was crystallised from rectified spirit in long needles, m p. 199-200°. (Found : C, 47.6 ; H, 3.5. $C_{12}H_{11}O_4Br$ requires C, 48.2 ; H, 3.7 per cent). The product formed an orange-yellow coloured sodium salt with 10% NaOH solution.

(*ii*) *Bromination with two moles Bromine* : 5-*Hydroxy*-6 : 8-*dibromo*-4 : 7-*dimethylcoumarin.*—5-Hydroxy-4 : 7-dimethylcoumarin (1.9 g.) in acetic acid (40 c.c.) was treated with bromine (3.2 g.) in acetic acid (32 c.c.) by heating on a steam-bath for 2 hours. The solid separating on cooling was crystallised from acetic acid in shining prisms (1.5 g.), m.p. 238-39° (decomp.). (Found : Br, 45.7. $C_{11}H_8O_3Br_2$ requires Br, 46.0 per cent). It gave a yellow sodium salt with alkali.

The *methyl ether* was prepared as usual by the dimethyl sulphate-acetone-K_2CO_3 method and crystallised from acetic acid in white shining needles (0.4 g.), m.p. 216°. (Found : Br, 44.1. $C_{12}H_{10}O_3Br_2$ requires Br, 44.2 per cent). This product on heating with 10% sodium hydroxide solution gave the original product back.

5-*Methoxy*-3 : 8-*dibromo*-4 : 7-*dimethylcoumarin.*—5-Methoxy-4 : 7-dimethylcoumarin (2 g.) in acetic acid (20 c.c.) was treated with bromine (3.2 g.) in acetic acid (32 c.c.) on a steam-bath for 2 hours. Product obtained was crystallised from acetic acid in shining needles (2 g.), m.p. 245-46°. (Found : Br, 44.1. $C_{12}H_{10}O_3Br_2$ requires Br, 44.2 per cent).

The same product was obtained when 5-methoxy-8-bromo-4 : 7-dimethylcoumarin (1.4 g) was brominated with one mole of bromine (0.8 g. in 8 c.c. of acetic acid) in hot.

4-*Methoxy*-7-*bromo*-3 : 6-*dimethylcoumarilic Acid.*—The above dibromocoumarin (0.6 g.) was refluxed with EtOH–NaOH (10%, 15 c.c.) for 3 hours. The product obtained on working up as usual was crystallised from acetic acid in small plates (0.2 g.), m.p. 269-70° (decomp.). (Found : C, 48.0, H, 3.4. $C_{12}H_{11}O_4Br$ requires C, 48.2 ; H, 3.7 per cent.). It dissolves in cold sulphuric acid to give a yellow solution which turns dark green on warming.

(*iii*) *Bromination with excess of Liquid Bromine* : 5-*Hydroxy*-3 : 6 : 8-*tribromo*-4 : 7-*dimethylcoumarin.*—5-Hydroxy-4 : 7-dimethylcoumarin (1.9 g.) was treated with liquid bromine (4 c.c.) and the reaction mixture was kept overnight. The excess of bromine was removed with sodium bisulphite and the product obtained was

crystallised from acetic acid in shining flakes (2.2 g.), m.p. 262-63°. (Found : Br, 56.5. $C_{11}H_7O_3Br_3$ requires Br. 56.1 per cent).

The *methyl ether*, prepared as usual by the dimethyl sulphate-K_2CO_3 method, was crystallised from acetic acid in shining faint yellow plates, m.p. 232-33°. (Found : Br, 54.5. $C_{12}H_9O_3Br_3$ requires Br, 54.4 per cent).

The same product (1.5 g.) was obtained when 5-methoxy-4 : 7-dimethylcoumarin (2 g.) was brominated with liquid bromine (5 c.c.) by heating on a steam-bath at 60°-70° for 2 hours.

4-*Methoxy*-5 : 7-*dibromo*-3 : 6-*dimethylcoumarilic Acid*.—The above coumarin (0.5 g.) was refluxed with EtOH – NaOH (10%, 20 c.c.) for 4 hours. The solid obtained on working up as usual was crystallised from acetic acid in tiny plates, (0.2 g.), m.p. 294-95°. (Found ; C, 38.0 ; H, 2.8. $C_{12}H_{10}O_4Br_2$ requires C, 38.1 ; H, 2.7 per cent). It dissolves in sulphuric acid in cold to give a yellow solution which turns dark green on warming.

The thanks of the authors are due to Miss G. Bhat for carrying out some preliminary work in this field. One of us (S. S. Lele) thanks the Government of India for the award of a Junior Research Scholarship.

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REFRACTOMETRIC STUDIES OF GLASS SYSTEMS. PLATINUM DISPERSED IN LINDEMANN GLASS

By Subodh Kumar Majumdar and Shyamal Kumar Mukherji

The mole refraction of platinum dispersed in Lindemann glass has been studied at different concentrations. The value of *R*, calculated from the Additivity Formula is found to be much higher than the value for pure platinum. This is an exception to the general rule that mole refraction of substances dissolved in glass media, is much smaller than their values in the crystalline state and in aqueous solutions, on account of strong deformation in the solid solution. The magnetic data of such systems also support a view which is contrary to strong deformation in such cases.

During investigations by the author on the subject of deformation of polar crystals and noble metals dispersed in different glass media (Wulff and Majumdar, *Z. physikal. Chem.*, 1936, **B,31**, 319 ; Majumdar and Sarma, this *Journal*, 1942, **19** 241 ; Majumdar and Palit, *ibid.*, 1942, **19**, 461 ; 1945, **22**, 317 ; Majumdar and Banerjee, *ibid.*, 1946, **23**, 171 ; Majumdar and Saha, *ibid.*, 1945, **22**, 147 ; Majumdar and Majumdar, *ibid.*, 1948, **25**, 251 ; Majumdar and Basu Chaudhury, *ibid.*, 1948, **25**, 301 ; Majumdar and Banerjee, *Indian J. Phys.*, 1946, **20**, 217) the mole refraction, X'ray diffraction, magnetic susceptibility and electrical conductivity of such glass systems have been studied and certain conclusions drawn from the results.

It has been found, as a result of refractometric measurements that Fajans' rule (Fajans and Joos, *Z. Physik*, 1921, **97**, 304) holds good in the case of glass systems as well. For example, Majumdar and Sarma (*loc. cit.*) found that the polarising power of different alkali cations on halogen ions, when the alkali halides are dissolved in B_2O_3-glass, follows the inequality :

$$Li^+ \rangle\ Na^+ \rangle\ K^+ \rangle\ Rb^+ \rangle\ Cs^+.$$

Reference may be made to a more recent paper of Fajans and Kreidl (*J. Amer. Cer. Soc.*, 1948, **31**, 105) who have shown that the value of *R*, the mole refraction which gives a measure of polarisability, for oxygen in silicate glasses decreases with increasing field strength of cations from Ba_2SiO_4 to Be_2SiO_4. It has also been shown that the polarisation of silicate glasses containing cations of noble gas type like Mg^{++} (8 outer electrons) is decidedly less than the polarisation in silicate glasses containing a non-noble gas type cation like Zn^{++} (18 outer electrons), and in the case of noble gas type cations, the polarisation may be expressed in terms of the inequality

$$2\ Be^{++} \rangle\ Si^{++++} \rangle\ 4/3\ Al^{+++} \rangle\ 2\ Mg^{++} \rangle\ 4\ Li^+,$$

which confirms Fajans' theory of deformation in the glasses investigated by these authors.

Since the conclusions drawn from the magnetic data of such glasses also run counter to those of mole refraction, it was thought desirable to study the refractome-

tric effect of a noble metal like platinum dispersed in a different glass like Lindemann glass, which is a lithium-beryllium borate glass and which possesses the power of dissolving platinum.

EXPERIMENTAL

Boric acid (extra pure quality) was recrystallised from hot water, conductivity water being used in the second crystallisation. It was dried at 100° for 3-4 days, until perfectly freed from water, as shown by anhydrous copper sulphate test with a solution made in absolute alcohol. Lithium carbonate and beryllium carbonate (both extra pure) were dried in an air-oven at about 200° for several hours. Chloroplatinic acid (Merck, extra pure), H_2PtCl_6, 6 H_2O was used.

An intimate mixture of 73% dried boric acid, 18% lithium carbonate and 9% beryllium carbonate was made and kept in a vacuum desiccator for several days. It was then heated in a platinum crucible in an electric furnace (800°-1000°) for 4 to 5 hours, until a clear homogeneous glassy melt was obtained. The melt was stirred from time to time with a thick platinum wire to expel the enclosed air bubbles. The resulting glass was carefully annealed. This precaution is necessary, as it is well known that borate glasses have the property of retaining traces of moisture even in high vacuum at 1000° (Wulff and Majumdar, *loc. cit.*). The previous history of a sample of glass, so far as annealing is concerned, is known to seriously modify its physical properties. The samples were stored in a vacuum desiccator. They were tested under cross Nicols in a Polarisation microscope to test for absence of strain. The glass, thus formed, was used as the the base for dispersing platinum.

An 1% solution of chloroplatinic acid was prepared in conductivity water and a calculated volume was pipetted into a clean platinum crucible. The solution was first evaporated on asbestos to dryness and a weighed amount of dry Lindemann glass was dropped into it. The crucible was maintained at 800°-1000° for 4 to 5 hours, until a clear melt was obtained. The samples were annealed in the same way as before. In this way, different samples of Lindemann glass containing varying quantities of dispersed platinum were prepared. The colour of the samples varied from light grey to dark. The maximum amount of platinum metal which could be taken by glass was found to be about 3%. Any platinum added in excess over this amount separated from the glass as metal.

Analysis of the Samples.—The potentiometric method of Müller and Weisbrod (*Z. anorg. Chem.*, 1926, 17, 156) for titrating the platinum was tried without success. The method gave good results in the case of gold (Majumdar and Basu Chaudhury, *loc. cit.*). Davis (Technical paper, 270, U.S. Bureau of Mines, p. 15) used a colorimetric method involving the use of $SnCl_2$, and Sandell ("Colorimetric determination of traces of metals", 1944, p. 352) recommended the method for titrating small amounts of platinum.

The method utilises the fact that when $SnCl_2$ reduces chloroplatinic acid, the colour varies from yellow to red, according as the platinum content is high or low. The intensity of colour is proportional to the acidity of the solution. Hence, a great care was taken to keep the acid concentration of the solution constant.

A standard solution of platinum was prepared by dissolving a weighed amount of dry pure platinum foil in aqua regia in a silica crucible. The excess of the acid was evaporated on a water-bath and 5 c.c. of concentrated HCl and 0.1 g. of pure NaCl were then added, and the solution was evaporated on the water-bath again. The residue was taken up with 20 c.c. of 1 : 1 HCl and diluted with distilled water to 100 c.c. This formed the stock solution. An one tenth dilute solution was prepared by suitable dilution, keeping the acid concentration constant.

A 10% solution of $SnCl_2$ in 2*N*-HCl was used. It was prepared by dissolving the calculated amount of pure metallic tin in concentrated HCl, evaporating on a water-bath in an atmosphere of CO_2 and making up the volume with standard acid.

A small glass sample was weighed and dissolved in aqua regia in a silica basin and evaporated as before. The residue was taken up with water and transferred to a measuring flask. Calculated amount of 1 : 1 HCl was then added together with 2 c.c. of standard $SnCl_2$ solution, and the solution diluted up to the mark ; 5 c.c. of this solution were taken in a Dubosq colorimeter and 5 c.c. of the standard solution to which also $SnCl_2$ had been added in the same way, were taken in the other arm. The transmittancy of the solutions was compared by using a high power bulb and blue filter and concentration of the solution was found out by adjusting against a particular length of the standard solution for the same transmittancy.

Determination of Density.—Densities of the samples were determined by the Floatation method, suggested first by Wulff and Heigl (*Z. physikal. Chem.*, 1931, **153A**, 187) and modified by Majumdar and Sharma (*loc. cit.*). The two liquids used were methylene iodide (heavy) and purified benzene (light).

Determination of the Refractive Index.—The refractive index of the glass pieces was determined by the Becke method as explained by Majumdar and Sharma (*loc. cit.*).

The following table records the results of analysis, density and refractive index determination of the glass samples.

TABLE I

% Pt (*p*).	Ref. index. (n_D)	Density. (*d*)	*r* for glass.	*r* for dispersed Pt.	Mol. ref. of Pt dispersed in glass.
0	1.5273	2.15870			
0.585	1.5281	2.15890	0.14260	0.1624	31.70
1.059	1.5287	2.15906	0.14280	0.1737	33.90
1.287	1.5290	2.15912	0.14290	0.1764	34.43
1.393	1.5294	2.15918	0.14295	0.17734	34.61
1.548	1.5296	2.15925	0.1430	0.1763	34.40
2.160	1.5302	2.15946	0.1431	0.1708	33.34
2.800	1.5312	2.15970	0.1433	0.1718	33.53

DISCUSSION

The specific refraction of the glass sample is calculated from the formula :

$$r = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{1}{d}$$

where r is the specific refraction of the sample.

The specific refraction r_1 of the dissolved platinum in the glass is calculated from the formula :

$$100r = p.r_1 + (100 - p)\, r_2,$$

where $(100-p)$ is the percentage of Lindemann glass and r_2, its specific refraction, it being understood that the latter remains constant in the samples. Any deviation from the additivity rule would point to mutual interaction between the constituents (Fajans' rule). The value for pure Lindemann glass is calculated to be 0.14248 ($n_D = 1.5273$ and $d = 2.15870$). Values of mole. refraction for platinum, found by multiplying the specific refraction by the atomic weight of platinum, are shown in Table I.

It is difficult to obtain the value for mol. refraction for pure platinum directly, being an opaque substance. The dielectric constant for a good conductor like platinum is meaningless, otherwise the value could be obtained from the well known Clausius-Mosotti equation. Lauch (*Ann. Physik*, 1944, **74**, 55) gives the following values for refractive index of platinum for optical frequencies : 1.83 for $\lambda = 5460$ Å and 1.92 for $\lambda = 5780$ Å and Pogany (*ibid.*, 1916, **49**, 531) gives a value 2.04 for $\lambda = 6000$ Å. The specific gravity of pure platinum may be taken as 21.45 at 20°. From these data, n_D for platinum may be taken as 2.00 (approx.). This gives a value 0.0233 for specific refraction for platinum and mole refraction comes out to be 4.54, which is small compared with the values obtained for platinum dispersed in glass. The results are therefore conflicting so far as refractometric data are concerned. In all the cases investigated so far, the mole refraction of dissolved salts is definitely less than the value in the crystalline state and in aqueous solution. This is also at variance with the subsequent work of Fajans and his co-workers on glass systems.

Majumdar and Bhattacharya (*Nature*, 1948, **161**, 684) have found that the diamagnetism of platinum dispersed in borax glass increases with an increase in the concentration of platinum which indicates an increase in the orbital path of electrons in platinum in the dispersed state.

A similar result may be anticipated in the present case. But the refractometric data run counter to previous observations with glass systems.

The slope of the (R-conc.) curve shows definitely positive slope which in the case of polar crystals, points to decreased dissociation, and consequently of stronger

deformation. This fact also in the present case has little theoretical significance, and would contradict the fact of larger mole refraction values observed.

Hence, platinum dispersed in Lindemann glass behaves anomalously, so far as its refractometric behaviour is concerned. The subject therefore possesses theoretical importance and the electrical conductivity of the metal in glass is being studied.

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POLAROGRAPHIC STUDY OF COBALT FERRICYANIDE COMPLEX

By B. D. Khosla and H. C. Gaur

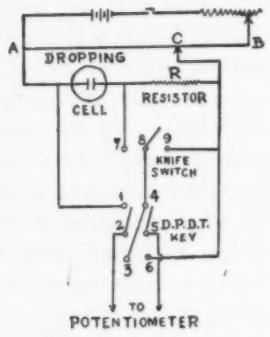
Polarographic study shows that cobalt ferricyanide has the composition $Co_3(Fe^{III}Cy_6)_2$.

The composition of cobalt ferricyanide by thermometric and conductometric methods has been studied by Gaur and Bhattacharya (*Proc. Nat. Acad. Sci. India*, 1950, **19A**, 45). In the present communication composition of the same compound has been studied polarographically.

Experimental

A 'manual' polarographic arrangement was set up. The circuit used is schematically shown in Fig. 1. A known E. M. F. could be applied to the dropping cell by a potentiometric arrangement. The current through the cell for a given value of the applied E. M. F. was obtained by measuring the potential drop across the standard resistor R (10,000 ohms) connected in series with the cell.

Fig. 1



AB was in the form of a Leeds and Northrup circular slide wire (resistance approx. 100 ohms) provided with a scale of 1,000 divisions to indicate the position of the movable contact C. For the sake of convenience, the total E. M. F. across AB was accurately adjusted to an integral number of volts. The E. M. F., E_a, applied to the cell could be varied by the movable contact C, and was given by the relationship :

$$E_a = E - \frac{RAC}{RAB} = E - \frac{AC}{AB}$$

By throwing D.P.D.T. key to the position 1 : 4, and the knife switch to the position 8 : 9, the total applied E. M. F. across AC for a given position of C could be measured with the potentiometer. This is almost equal to the E. M. F., E_a, applied to the cell. The correct value of the applied E.M.F. was obtained by subtracting from the E. M. F. across AC the measured potential drop across the standard resistor. The potential drop across the cell could be verified by keeping the D. P. D. T. key in the same position, and changing the knife switch to the position 7 : 8.

For measuring the current through the cell, the D. P. D. T. key was thrown to the position 3 : 6, and the knife switch to the position 7 : 8. This measured the potential drop across the resister R, from which the current in the circuit was calculated.

Ilkovic (*Coll. Czech. Chem. Comm.*, 1936, 8, 13), and Brdicka (*ibid.*, 1936, 8, 419) have shown that during the formation of each mercury drop the current increases many fold, and its maximum value just before the drop falls is several times greater than its minimum value at the beginning of the drop formation. The diffusion $\bar{i}$ in the Ilkovic equation :

$$\bar{i} = 605nD^{\frac{1}{2}}.\ Cm^{\frac{2}{3}}t^{\frac{1}{6}}$$

[where $\bar{i}$=average current in micro-amperes, n=No. of faradays required per mole of electrode reaction, D=diffusion coefficient of the electro-reducible substance, C=conc. of the above in millimoles/litre, m=mg of mercury flowing through the capillary per second and t=drop time in seconds] refers to the average value of the current during the life of each drop. Exact determination of this average current is extremely difficult. It is known (Kolthoff and Lingane, "Polarography", p. 38, 1941) that this average current is 6/7th of the maximum current. In the experimental determination of the potential drop across the resistor, the opposing E. M. F. applied had a value such that the galvanometer needle approached the zero position when the drop just fell (corresponding to the maximum current in the circuit). Since an ordinary galvanometer is too sluggish to register the change in the current in the life of a drop, the observed current is somewhat smaller than the true maximum current, and will not be much different from the average current. The maximum current and the average current, however, are both proportional to the concentration of the electro-reducible substance in the solution, and a substitution of the observed value of the current, thus obtained for the average current, is not of much consequence in the interpretation of the results obtained.

The capillary for the dropping mercury electrode was made by carefully drawing a jet from the finest thermometer tubing available, so that the internal diameter of the jet tip was of the order of 0.03 mm., and the narrowest part was uniform in bore over 2-3 cm. from the tip. The correct bore could only be obtained after a number of trials when with a given capillary the drop time of 3 to 6 secs. in N/10-KCl solution, could be adjusted by a suitable adjustment of pressure over the dropping mercury.

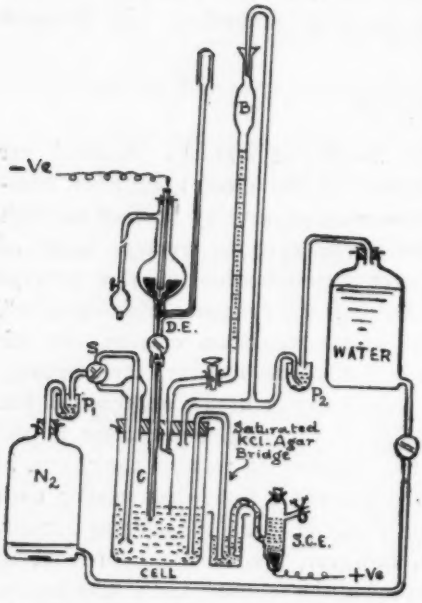
A thick walled 100 c.c. Pyrex distillation flask was used as a mercury reservoir with a stop-cock fused into its bottom, the lower end of the stop-cock being butt-jointed to a dropping capillary with a small piece of transparent plastic tubing. The pressure over the dropping mercury could be adjusted by flowing in air with a rubber pressure bulb attached to the side tube of the flask. The applied pressure could be obtained from the level of mercury in a side capillary tube fused to the bottom of the reservoir.

The same dropping capillary, with almost the same pressure on mercury, was used throughout the work.

For the polarographic titration work, the dropping electrode served as the cathode, and the anode was a depolarised electrode (saturated calomel half cell).

Since it is well known that oxygen is easily reduced at the dropping electrode, it is necessary to remove it from the solutions used in the titrations. This was done by bubbling purified nitrogen through the solutions before starting a titration and the titrations were also performed in an atmosphere of nitrogen. For thorough mixing, after each addition from the burette, compressed nitrogen was bubbled through the solution. The arrangement shown in Fig. 2 was used and was quite convenient for the titration work.

FIG. 2



D.E. = dropping electrode; C = capillary. By manipulation of the 3-way stop-cock S, N_2 could be bubbled into the soln. or hassed over it in the cell, C. The microburette, B, previously flushed with nitrogen, contained the titrant. A number of purifies (only P_1, P_2 shown) were inserted in the path of N_2.

To minimise the dilution effect, the titrant was made about 25 times more concentrated than the solution to be titrated. The titrant was added through a microburette graduated to read 0.02 c.c. The 'diffusion current' obtained after each addition of the titrant was corrected for the small dilution effect by multiplying the observed value by the factor $(V+v)/V$, where v is the volume of the titrant added up to a given stage, and V is the originally taken volume of the solution to be titrated (cf. Kolthoff and Lingane, *loc. cit.* p.463; Bhattacharya and Gaur, this *Journal*, 1948, **25**, 27).

To suppress maxima in the *c-v* curves, 0.5 c.c. of 0.05% gelatine solution was added to every 40 c.c. of the solution to be titrated. To eliminate the migration component of the 'limiting current', *N*/10-KCl was used as a "supporting electrolyte" throughout the work.

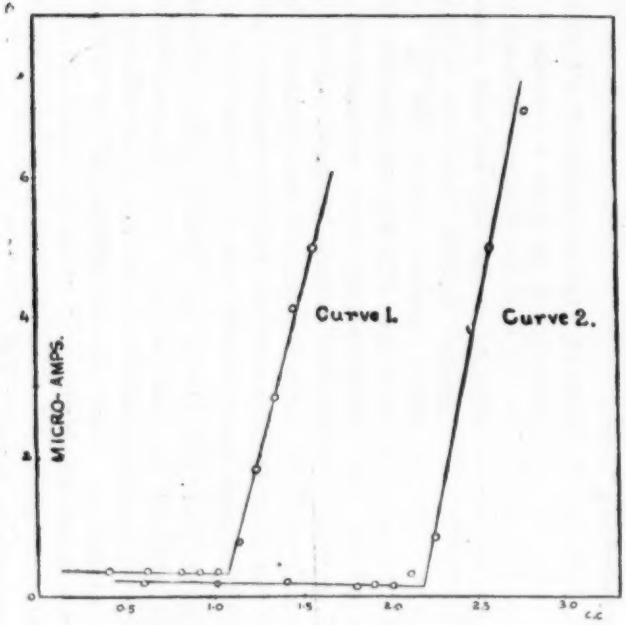
DISCUSSION

Results of the "amperometric titrations" are shown graphically in Figs. 3 and 4. The titrations were done at 35° using $E_a = -0.8$ volt and $R = 10{,}000$ ohms.

The *c-v* curve of cobalt chloride was first studied using a Leeds and Northrup electro-chemograph, and, later on, the manual polarograph. The value of $E_{\frac{1}{2}}$ for cabalt (-1.18 volts *vs.* S. C. E.) was found to be the same in both cases. The polarogram of 0.002*M*-cobalt chloride solution in *N*/10-KCl is shown in Fig. 5.

It will be seen from the polarogram that up to a dropping electrode potential of -0.9 volt (*vs.* S. C. E.), the electrolysis of cobalt chloride solution does not

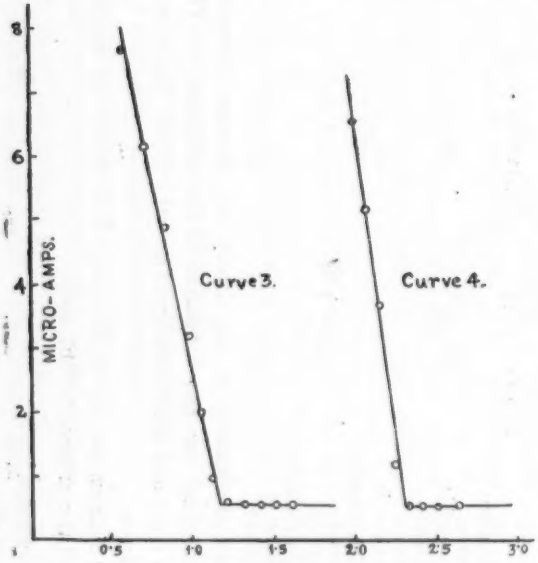
FIG. 3



Curve 1 : 100.1 millimolar $K_3Fe(Cy)_6$ added to 40.0 c.c. of 4.0 millimolar $CoCl_2$.

Curve 2 : 100.1 millimolar $K_3Fe(Cy)_6$ added to 40.0 c.c. of 8.0 millimolar $CoCl_2$.

FIG. 4

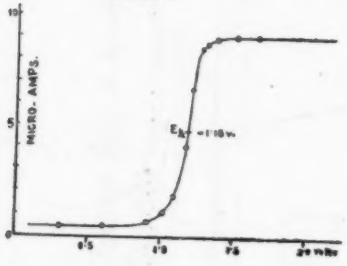


Curve 3 : 200.4 millimolar $CoCl_2$ added to 40.0 c.c. of 3.995 millimolar $K_3Fe(Cy)_6$.

Curve 4 : 200.4 millimolar $CoCl_2$ added to 40.0 c.c. of 7.99 millimolar $K_3Fe(Cy)_6$.

commence. The small residual current in the beginning is due to the KCl. In case of potassium ferricyanide ($E_{\frac{1}{2}} = +0.2$ *vs.* S.C.E.), a diffusion current will be obtained from all negative values of the applied E.M.F. Therefore if we apply a potential of -0.8 volt *vs.* S.C.E. to the dropping electrode with cobalt chloride in the cell and add potassium ferricyanide solution from the burette, only a feeble residual current due to the carrying electrolyte, KCl, will be obtained, because the cobalt chloride is not decomposed at this value of the applied potential. After the equivalence point, the free potassium ferricyanide present will give rise to a diffusion current, which according to the Ilkovic equation (*loc. cit.*), will increase almost linearly with its concentration.

FIG. 5



If the titrations are done in the reverse way (adding cobalt chloride to potassium ferricyanide), applying the same potential to the dropping electrode, as long as there is potassium ferricyanide present in the cell, the current will decrease almost linearly with the addition of cobalt chloride solution till the equivalence point, whereafter, there will be only a feeble residual current.

The observed titre values and those calculated assuming the formation of the more probable compounds are shown in Table I.

TABLE I

	Calculated titre values assuming $KCo[Fe^{III}Cy_6]$.	Calculated titre values assuming $Co_3[Fe^{III}(Cy)_6]_2$	Obs. titre value.
1. 100.1 m/molar potassium ferricyanide added to 4 m/molar cobalt chloride	1.60 c.c.	1.065 c.c.	1.08 c.c.
2. 100.1 m/molar potassium ferricyanide added to 8 m/molar cobalt chloride	3.20	2.13	2.15
3. 200.4 m/molar cobalt chloride added to 3.995 m/molar potassium ferricyanide	0.79	1.18	1.17
4. 200.4 m/molar cobalt chloride added to 7.99 m/molar potassium ferricyanide	1.58	2.36	2.33

The titre values, as obtained by the direct and reverse titrations, correspond closely to those required for the formation of the compound $Co_3(FeCy_6)_2$ as previously reported by Gaur and Bhattacharyya (*loc. cit.*) from thermometric and conductrometric titrations.

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TRANSFORMATION OF BIGUANIDES INTO DICYANDIAMIDINES

By Nakuleswar Kundu

The kinetics of the hydrolytic change of some biguanides into the corresponding dicyandiamidines have been studied at two different temperatures with a view to studying the influence of substituents on the rate of transformation.

It has been described (Kundu, *Science & Culture*, 1949, **15**, 240; 1950, **15**, 449; Kundu and Rây, *Proc. Indian Sci. Cong.*, 1952, III, p. 100; this *Journal*, 1952, **29**, 811), that N^1-*p*-sulphonamidophenylbiguanide in acid solution undergoes a gradual change into the corresponding dicyandiamidine at the ordinary temperature. Since the rate of transformation varied with the nature of the substituent in the biguanide molecule, it was considered worthwhile to study the kinetics of the reaction in a quantitative manner. As during the course of the transformation an equivalent amount of ammonia is liberated, the rate of change can be easily followed from the change in the acid concentration of an aqueous solution of the biguanide hydrochloride containing a definite initial quantity of acid.

It has been found that the change follows the equation for unimolecular reaction,

$$kt = \ln a/a-x.$$

By plotting the values of log $a/a-x$ against the time intervals, t, a more or less straight line curve is obtained showing that the reaction is unimolecular.

The velocity constants at 32° and 46° were determined.

In the previous publications (*loc. cit.*), it has been noted that the presence of sulphonamido group in the *para* position of the phenyl radical is essential for the rapid hydrolytic change of the biguandie. The transformation rate remains practically unaffected even when the hydrogen atoms of the sulphonamido group are replaced by methyl, ethyl, phenyl, dimethyl and diethyl radical. But the change is more or less strongly inhibited by an alkyl, dialkyl or aryl substitution in the N^5-position of the biguanide.

In order to make a quantitative study of the effect of these substituents at different positions on the rate of transformation, the present work was undertaken. Measurements were made on the following compounds and the results are shown in Tables I-VIII.

(1) N^1-*p*-Sulphonamidophenylbiguanide.
(2) N^1-*p*-Methylsulphonamidophenylbiguanide.
(3) N^1-*p*-Ethylsulphonamidophenylbiguanide.
(4) N^1-*p*-Phenylsulphonamidophenylbiguanide.
(5) N^1-*p*-Dimethylsulphonamidophenylbiguanide.
(6) N^1-*p*-Diethylsulphonamidophenylbiguanide.
(7) N^1-*p*-Sulphonamidophenyl-N^5-ethylbiguanide.
(8) N^1-*p*-Sulphonamidophenyl-N^5-diethylbiguanide.

EXPERIMENTAL

The biguanide solution (0.05*M*, 100 c. c.) was taken in a 200 c. c. volumetric flask and diluted approximately to 175 c. c. and the solution kept in an electrically regulated thermostat at 32° (±0.05°) for 2 to 3 hours; to this 11.05 c. c. of hydrochloric acid (1.809 *N*), also at 32°, were added with shaking and then the volume was made up to 200 c. c. with water at 32°. The mixture (5 c. c.) was then taken by means of a pipette, diluted with 20 c. c. of water and titrated immediately with standard alkali (*N*/50) using Weslow's indicator. The flask with the solution was left in the thermostat and 5 c. c. of it were withdrawn at different intervals of time and titrated as before. Another series of measurements was made similarly at 46°.

TABLE I

Compound No. 1.

Temperature = 32°.			Temperature = 46°.		
Time.	Titre values in *N*/50-alkali.	$k_{32} \times 10^7$/sec. (Uni).	Time.	Titre values in *N*/50-alkali.	$k_{46} \times 10^6$/sec. (Uni).
0 hr.	25.00 c.c.	...	0 hr.	25.00 c c.	...
3	24.85	22.59	3	24.65	5.33
9	24.70	15.21	9	24.15	4.51
21	24.50	11.04	18	23.60	3.91
33	24.15	10.74	30	23.05	3.46
51	23.95	10.21	48	22.45	3.03
75	23.55	9.77	72	21.80	2.77
99	23.20	9.53			
123	22.90	9.25			
147	22.60	9.15			
171	22 30	9.19			
195	22.05	9 10			

From the table, k_{32} (mean) $\times 10^7$/sec. = 9.77. Graphically, $k_{32} \times 10^7$/sec. = 8.77.

From the table, k_{46} (mean) $\times 10^6$/sec. = 3.29. Graphically, $k_{46} \times 10^6$/sec = 2 80.

TABLE II

Compound No. 2.

Temperature = 32°.			Temperature = 46°.		
Time.	Titre values in *N*/50-alkali.	$k_{32} \times 10^7$/sec. (Uni).	Time.	Titre values in *N*/50-alkali.	$k_{46} \times 10^6$/sec. (Uni).
0 hr.	25.00 c. c.	...	0 hr.	25.00 c.c.	...
4	24.90	11.19	3	24 70	4.56
24	24.55	8.66	6	24.40	4.68
48	24.10	8.99	9	24.20	4.23
72	23.65	9.39	24	23 20	3 93
96	23.30	9.19	32	22.70	3.98
120	23.00	8.93	50	21.95	3.72
168	22 45	8.67	74	21.30	3.37
216	22.00	8.41			
264	21.65	8.08			
312	21 35	7.81			

From the table, k_{32} (mean) $\times 10^7$/sec. = 8.68. Graphically, $k_{32} \times 10^7$/sec. = 8.59.

From the table, k_{46} (mean) $\times 10^6$/sec. = 4 07. Graphically, $k_{46} \times 10^6$/sec. = 3.99.

TABLE III

Compound No. 3.

Temperature = 32°.			Temperature = 46°.		
Time.	Titre values in N/50-alkali.	$k_{32} \times 10^7$/sec. (Uni).	Time.	Titre values in N/50-alkali.	$k_{46} \times 10^6$/sec. (Uni).
0 hr.	25.00 c. c.	...	0 hr.	25.00 c.c.	...
4	24.85	16.94	3	24.70	4.56
24	24.50	9.65	6	24.45	4.26
48	24.00	10.09	9	24.20	4.23
72	23.55	10.19	24	23.20	3.93
96	23.20	9.83	32	22.70	3.98
120	22.90	9.48	50	21.95	3.72
168	22.30	9.87	74	21.30	3.37
216	21.80	9.23			
264	21.50	8.64			
312	21.25	8.16			
From the table, k_{32} (mean) $\times 10^7$/sec. = 9.45.			From the table, k_{46} (mean) $\times 10^6$/sec. = 4.00.		
Graphically, $k_{32} \times 10^7$/sec. = 9.59			Graphically, $k_{46} \times 10^6$/sec. = 3.97.		

TABLE IV

Compound No. 4.

Temperature = 32°.			Temperature = 46°.		
Time.	Titre values in N/50-alkali.	$k_{32} \times 10^6$/sec. (Uni).	Time.	Titre values in N/50-alkali.	$k_{46} \times 10^6$/sec. (Uni).
0 hr.	25 00 c c.	...	0 hr.	25.00 c.c.	...
3	24.90	1.49	3	24 60	6.12
22	24.50	1 05	6	24.25	5.92
46	23 95	1.11	9	23.95	5.68
70	23.50	1.09	24	22.85	4.88
94	23.10	1.07	32	22.35	4.79
118	22.80	1.02	50	Precipitation occurs.	
166	Precipitation occurs.				
From the table, k_{32} (mean) $\times 10^6$/sec = 1.14.			From the table, k_{46} (mean) $\times 10^6$/sec = 5.31.		
Graphically, $k_{32} \times 10^6$ sec. = 1.03.			Graphically, $k_{46} \times 10^6$/sec. = 4.93.		

TABLE V

Compound No. 5.

Temperature = 32°.			Temperature = 46°.		
Time.	Titre values in $N/50$-alkali.	$k_{32} \times 10^7$/sec. (Uni).	Time.	Titre values in $N/50$-alkali.	$k_{46} \times 10^6$/sec. (Uni).
0 hr.	25.00 c.c.	...	0 hr.	25.00 c. c.	...
4	24.85	16.94	3	24.70	4.56
24	24.50	9.65	6	24.45	4.26
48	24.00	10.09	9	24.20	4.23
72	23.55	10.19	24	23.20	3.93
96	23.20	9.83	32	22.70	3.98
120	22.85	9.76	50	21.95	3.72
168	22.30	9.35	74	21.30	3.37
216	21.90	8.81			
264	21.55	8.45			
312	21.25	8.16			

From the table, k_{32} (mean) $\times 10^7$/sec. = 9.25.

Graphically, $k_{32} \times 10^7$/sec. = 9.88.

From the table, k_{46} (mean) $\times 10^6$/sec. = 4.00.

Graphically, $k_{46} \times 10^6$/sec. = 3.97.

TABLE VI

Compound No. 6.

Temperature = 32°.			Temperature = 46°.		
Time.	Titre values in $N/50$-alkali.	$k_{32} \times 10^7$/sec. (Uni).	Time.	Titre values in N/50-alkali.	$k_{46} \times 10^6$/sec (Uni).
0 hr.	25.00 c.c.	...	0 hr.	25.00 c.c.	...
4	24.85	5.94	3	24 65	5.33
24	24.50	9 65	6	24.35	5.09
48	24.00	10.09	9	24.15	4.51
72	23.65	9.35	24	23.20	3.93
96	23.35	8	32	22.75	3.88
120	23.10	8.39	50	22.15	3.38
144	22.90	7.90	74	21.50	3.08
192	22.55	7.20			
240	22.25	6.71			
288	21.95	6.61			

Form the table, k_{32} (mean) $\times 10^7$/sec. = 8.30.

Graphically, $k_{32} \times 10^7$/sec. = 9.49.

From the table, k_{46} (mean) $\times 10^6$/sec. = 3.75.

Graphically, $k_{46} \times 10^6$/sec. = 3.84.

TABLE VII

Compound No. 7.

Temperature = 46°.

Time.	Titre values in $N/50$-alkali.	$k_{46} = 10^7$/sec. (Uni).
0 hr.	25.00 c. c.	...
3	25.00	...
27	24.90	1.66
75	24.70	1.83
147	24.30	2.25
243	23.85	2.33

From the table, k_{46} (mean) $\times 10^7$/sec. = 2.01.

Graphically $k_{46} \times 10^7$/sec. = 2.39.

TABLE VIII

Compound No. 8.

Temperature = 46°.

Time.	Titre values in $N/50$-alkali.	$k_{46} \times 10^7$/sec. (Uni).
0 hr.	25.00 c. c.	...
3	25.00	...
27	24.90	1.66
75	24.70	1.83
147	24.45	1.74
243	24.10	1.78

From the table, k_{46} (mean) $\times 10^7$/sec. = 1.75.

Graphically, $k_{46} \times 10^7$/sec. = 1.76

(The mean values of k, as calculated from the tables, were obtained by ignoring the results of first 2 or 3 measurements for reasons stated in the discussion.)

At 32°, the compounds (7) and (8) showed very little change even after a day or two.

Table IX presents a comparative view of the specific reaction rates of the different compounds.

TABLE IX

(With graphical values of k)

Compound No.	1	2	3	4	5	6	7	8
$k_{32} \times 10^7$/sec.	8.77	8.59	9.59	10.30	9.88	9.49	—	—
$k_{46} \times 10^7$/sec.	28.0	39.90	39.70	49.30	39.70	38.40	2.39	1.76

DISCUSSION

From an examination of the results recorded in the tables it is clear that in the beginning the difference in titre values is extremely small which obviously accounts for the very large deviation of the k values calculated on the unimolecular basis. Thereafter the values become more or less equal though slight variations still persist. This can presumably be attributed to the fact that the H^+ ion, which serves as a catalyst in the hydrolytic reaction, is removed continuously by combination with ammonia, one of the products of hydrolysis.

$$R-NH-\underset{\underset{NH}{\|}}{C}-NH-\underset{\underset{NH}{\|}}{C}-NH_2+H_2O \xrightarrow{H^+} R-NH-\underset{\underset{O}{\|}}{C}-NH-\underset{\underset{NH}{\|}}{C}-NH_2+NH_3 \quad \ldots \quad (i)$$

$$NH_3+H^+ \longrightarrow NH_4^+ \quad \ldots \quad \ldots \quad (ii)$$

It was in fact previously observed that the time required for the conversion of N^1-*p*-sulphonamidophenylbiguanide decreased with the increase in the concentration of the acid used. Unless the acid strength in the reaction mixture be maintained at a high value, the concentration of the catalyst will effectively change and will thereby progressively reduce the specific reaction velocity to a certain extent. If it were possible to work with more concentrated solutions of biguanide, the abnormally large variations of the k values for the first 2 or 3 measurements could be more or less eliminated. But this was not possible, as in that case the product of hydrolysis, *i.e.*, the dicyandiamidine salts, being difficultly soluble, separated out from the solution. Nevertheless, inspite of all these limitations imposed on the study of the change, the results unmistakably demonstrate the unimolecular nature of the reactions.

Compounds (7) and (8) have no measureable velocity at 32° showing that the substitution at N^5-position of N^1-*p*-sulphonamidophenylbiguanide strongly retards the rate of hydrolysis. There is no such conspicuously marked variation, however, in the rate of transformation by substitution in the *p*-sulphonamido group at N^1_a-position. An aryl (phenyl) substitution at this position, however, exercises a somewhat greater accelerating influence than the alkyls and dialkyls (methyl, ethyl, dimethyl and diethyl) (cf. compounds 1-6). This is particularly noticeable at the higher temperature of 46°. The temperature variation of the unsubstituted compound (No. 1) also appears to be somewhat lower. Compounds (3), (5) and (6) have almost the same values for k at both 32° and 46°. That is, the substitution of ethyl, dimethyl and diethyl at the sulphonamido group exercises the same influence on the rate of hydrolysis of the biguanide molecule.

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STUDIES ON THE BEHAVIOUR OF BI-UNIVALENT SALTS IN AQUEOUS SOLUTION. PART VII. COPPER ACETATE

By S. C. Sircar, S. Aditya and B. Prasad

Cells of the type : $Hg\left|Hg_2Ac_2, CuAc_2(c), HAc\ (c_1)\right\|\overset{Sat.}{KCl}\left\|HAc\ (c_2), BaAc_2(c), Hg_2Ac_2\right|Hg$ were studied.

The values of c_1 and c_2 were selected in such a way that the p_H values of the solutions of the cell on the two half cells were the same. The presence of acetic acid was necessary to suppress the hydrolysis of copper acetate and barium acetate. Assuming that the liquid junction potential to be negligible and barium acetate to be completely dissociated within the range of concentration studied (0.01-0.1*M*), the concentration of free acetate ion in copper acetate was calculated from the knowledge of the E.M.F. of the cell and some assumptions about the activity coefficient. The dissociation of copper acetate was found to take place in two stages :

$$(1)\ CuAc_2 \rightleftarrows CuAc^+ + Ac^-,$$
$$(2)\ CuAc^+ \rightleftarrows Cu^{++} + Ac^-$$

The dissociation constants were found by the method of approximations. Three approximations were necessary to give exact results which are

$K_1\ (CuAc_2 \rightleftarrows CuAc^+ + Ac^-) = 1.25 \times 10^{2}$ and $K_2\ (CuAc^+ \rightleftarrows Cu^{++} + Ac^-) = 4 \times 10)^{-3}$

The colour of copper salts and variation with concentration and addition of alkaline earth salt of same anion have been of much interest to the scientists for years. Colour change produced by addition of alkali salt was noted and explained on the assumption of incomplete dissociation and complex formation (*J. Chem. Soc.*, 1902, **81**, 7391). Sidgwick and Tizard (*ibid.*, 1910, **97**, 957) measured molecular depth of colour and conductance of copper salt of both organic and inorganic acids. From such observations they infer that in case of organic salts, only the first stage of dissociation proceeds within the range of concentration of 5-40 litres per g. mole. But they themselves admit that their line of argument may not be absolutely correct as the ionic mobility calculated by them were too high. So the present piece of work has been undertaken to throw some more light on the true behaviour of copper acetate in aqueous medium.

Experimental

In order to stop the hydrolysis, a solution of copper acetate was prepared in 0.4 to 0.5*N* acetic acid. After five days the solution was estimated for copper by the usual iodimetric method and for acetic acid by alkalimetric method.

An approximate 0.5*M* solution of barium acetate was prepared and allowed to stand for four days. Its p_H was measured and found to remain constant. Barium was estimated as barium sulphate by gravimetric method.

Solutions of 0.01, 0.02, 0.04, 0.06, 0.08 and 0.1*M* were prepared out of both copper acetate and barium acetate. Requisite quantity of acetic acid was added to barium acetate before making it to the volme in order to equalise its p_H with that of the corresponding copper acetate. These solutions were used in the cells.

The cells and bridges were of the same type as used earlier (this *Journal*, 1951, 28, 683). Two half cells of the type, $Hg \mid Hg_2Ac_2$, $CuAc_2$ (c) HAc (c_1) and $Hg \mid Hg_2Ac_2$, $BaAc_2$ (c) HAc (c_2) were set up. Two similar half elements were checked before use by the method described in previous papers of the series. Then two dissimilar half elements of the same concentration were joined through saturated KCl bridge. The readings were taken after about 3 hours. The E. M. F. of the cell remained constant even for twenty four hours. Duplicates agreed within 0.1mv. All the readings were taken at room temperature which varied from 29° to 33° in course of a number of days. Some readings were also taken with half-saturated salt bridges. The E M.F. value for a particular cell with saturated and half-saturated bridge did not differ by more than 0.25 mv. Bjerrum's method of correction was not used as it was not found trustworthy in this laboratory (this *Journal*, 1952, 29, 925). So E.M.F. with saturated bridges were only used for calculation. All the E.M.F. values were reduced to that for 30° by the use of the equation,

$$\frac{E_t}{E_{30}} = \frac{273+t}{273+30}.$$

TABLE I

Conc. of $CuAc_2$ & $BaAc_2$ in g. moles/litre. (c)	E. M. F. with sat. KCl bridge.	Temp.	E. M. F. with sat. bridge at 30°.	Activity of Ac^- ion in $CuAc_2$ as calc. from E. M. F. with sat. bridge at 30°.
0.01*M*	0.01020	30°	0.01020	0.01148
0.02	0.01338	32.5°	0.01326	0.01939
0.04	0.01608	30°	0.01608	0.03280
0.06	0.01753	29°	0.01758	0.04442
0.08	0.01935	29.5°	0.01938	0.05375
0.10	0.01990	30.5°	0.01987	0.06463

TABLE II

Conc. of $CuAc_2$ & $BaAc_2$ in g. moles/litre (c)	K_2.	μ.	α.	β.	K_1.
0.01 *M*	4×10^{-3}	0.0165	0.9625	0.3558	0.166*
0.02	Do	0.0273	0.9120	0.2490	0.1285
0.04	Do	0.0470	0.8428	0.1780	0.1194
0.06	Do	0.0630	0.8074	0.1412	0.1287
0.08	Do	0.0750	0.7530	0.1270	0.1140
0.10	Do	0.0916	0.7499	0.1209	0.1338

Mean K_1=0.125

*Neglected while taking mean.

DISCUSSION

The E.M.F. of the cell,

$Hg \mid Hg_2Ac_2,\ CuAc_2(c),\ HAc(c_1) \| sat.\ KCl \| HAc(c_2),\ BaAc_2,\ Hg_2Ac_2 \mid Hg,$

is given by $E = \frac{RT}{F} \log \frac{a}{a_1} \frac{(\text{activity of } Ac^- \text{ ion in } BaAc_2)}{(\quad\ \text{,,}\quad\ \text{,, } Ac^- \text{ ion in } CuAc_2)}$ ... ... (1)

The barium acetate has been assumed to be completely dissociated. Activity coefficient of acetate ion and chloride ion was taken to be the same at the same ionic strength. So with these assumptions activity coefficient of acetate ion in barium acetate was determined by the method followed in previous papers of the series. It was substituted in the equation (1) and a_1, the activity of the copper acetate was calculated. At lower concentrations a_1 was found to be greater than the molar concentration of copper acetate. But as the concentration goes higher, a_1 becomes less than the molar concentration. The value becomes so low that the activity coefficient alone cannot account for this (vide Table I). So the two-stage dissociation for copper acetate has to be taken into account.

$$\underset{(1-\alpha)c}{CuAc_2} \rightleftharpoons \underset{\alpha c(1-\beta)}{CuAc^+} + \underset{\alpha c.}{Ac^-}$$

$$\uparrow\downarrow$$

$$\underset{\alpha\beta c}{Cu^{++}} + \underset{\alpha\beta c}{Ac^-}$$

$$K_1 = \frac{\alpha^2(1-\beta^2)cf_-^2}{1-\alpha} \quad \text{... ... (2)}$$

$$K_2 = \frac{c\alpha\beta(1+\beta)f_{++}}{1-\beta} \quad \text{... ... (3)}$$

$$a_1 = \alpha c(1+\beta)f_- \quad \text{... ... (4)}$$

(f_- = activity coeff. of Ac^- ion;
f_{++} = " " " Cu^{++} ";
f_+ = " " " $CuAc^+$ ").

The values of K_1 and K_2 become easier to calculate if we assume $f_- = f_+$. From the data available it is not possible to calculate K_1 and K_2 straight off. To begin with, the first stage of dissociation was assumed to be complete and K_2 (value given below) was roughly calculated on the assumption (*i*) that the ionic strength was roughly 3*c* and (*ii*) that activity coefficients of same valency type ions are the same at the same ionic strength.

Conc. of $CuAc_2$ (c) (in g. mol.) ...	0.01	0.02	0.04	0.06
Values of $K_2 \times 10^3$	3.961	2.713	1.276	0.3924

The gradual increase in the value of K_2 can be explained only by the assumption that the first stage of dissociation proceeds towards completion with dilution. So the value of K_2 cannot be less than 3.96×10^{-3} or roughly 4×10^{-3}. So, in order to ascertain the correct value of K_1 and K_2 arbitrary plausible values were given to K_2 varying from 4×10^{-3} to 8×10^{-3}. The value of K_1 was calculated for each value of K_2 from each of the concentration cells. The value of K_2 which gave the most concordant value of K_1 (in all the cells) was taken to be the right value for K_2. The calculations were done as follows :

One cell of the type :

$Hg \mid HgAc_2, CuAc_2\ (c), HAc\ (c_1) \parallel$ sat. $KCl \parallel HAc\ (c_2), BaAc_2\ (c), Hg_2Ac_2 \mid Hg$ is considered for illustration. The activity of acetate ion in copper acetate, a_1, was determined as described earlier. Now,

$$a_1 = \alpha c(1+\beta) f_- - Bf_- \quad \ldots \quad \ldots \quad \ldots \quad (5)$$

Equation (3) can be written as

$$\beta = \frac{K_2}{K_2 + Bf_{++}} \quad \ldots \quad \ldots \quad \ldots \quad (6)$$

Now, a rough value of 'f_-' on the basis of complete dissociation can be found as described earlier in this paper. So it becomes possible to get a rough value of B from the equation (5) by the method used in the previous papars of the series. A rough value of 'f_{++}' can also be obtained if we assume that the copper acetate is completely dissociated. Giving a definite value to K_2, β is roughly calculated from the equation (6) and with the value of β and B known, α is calculated. With the rough value of α and β, a more accurate value of ionic strength than $3c$, assumed before, is calculated from the equation

$$\mu = \alpha c(1+\beta) \quad \ldots \quad \ldots \quad \ldots \quad (7)$$

With this value of μ a new value of 'f_-' and 'f_{++}' can be found by the same method as above. With the values of f_- and f_{++}, new values of β and α and ionic strength are found. This process is repeated till there is no further change in the value of α and β. Three approximations were found to be enough. For the given value of K_2, K_1 is thus found for the cell under consideration. This is repeated in case of other cells. That value of K_2 is selected which gives nearly the same value of K_1 in all the cells. The most concordant value of K_1 is found when K_2 is taken to be 4×10^{-3}. In Table II only the calculations with K_2 equal to 4×10^{-3} are given. The mean value of K_1 is found to be 1.25×10^{-1}.

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AMPEROMETRIC TITRATIONS WITH POTASSIUM FERROCYANIDE. PART I. DETERMINATION OF ZINC

By Baldev Khosla and Harish C. Gaur

The amperometric titrations of oxygen-free (1.5 to 4.5 millimolar) solutions of zinc in $N/10$ potassium chloride medium with standard potassium ferrocyanide have been carried out at a dropping mercury electrode potential of −1.18 volts *vs* S. C. E. Gelatine was used as a 'maximum suppressor'. It was found that p_H of the zinc solution should not be lower than 2.1. The titrations are best done at 60° when the results obtained are within 1 to 2.5% of the calculated values.

In the volumetric titration of a dilute solution of zinc with potassium ferrocyanide, using diphenylamine as an internal indicator, the change of colour at the end-point is not very sharp. Several attempts have been made for the amperometric determination of zinc by potassium ferrocyanide under different experimental conditions. Spalanka (*Coll. Czech. Chem. Comm.*, 1939, **11**, 146) carried out the titrations of potassium ferrocyanide with zinc in 0.2 N hydrochloric acid solution at a potential of −1.2 volts where zinc yielded a diffusion current. He recommended that zinc should be added to potassium ferrocynide and the product of reaction was found to correspond to $K_2Zn_3(FeCy_6)_2$. Nimmer, Hamm and Lee (*Anal. Chem.*, 1950, **22**, 790) carried out the direct amperometric titration of zinc with potassium ferrocyanide in a supporting electrolyte of 1.7M ammonium acetate at an applied potential of −1.4 volts *vs.* S. C. E. The precipitate formed approached the composition $Zn_2[FeCy_6]$.

The present work deals with the possibility of the direct estimation of small amounts of zinc with potassium ferrocyanide under acid conditions. The optimum experimental conditions for such titrations have been worked out.

Experimental

The 'manual' polarographic arrangement (Khosla and Gaur, this *issue*, p. 622) was used for carrying out the amperometric titrations. Dropping mercury electrode was used as the cathode and a saturated calomel electrode (S. C. E.) as the external reference electrode. All the solutions were rendered free of dissolved oxygen by bubbling purified nitrogen. The zinc solutions to be titrated were $N/10$ with respect to the carrying electrolyte, KCl, and contained 0.5 ml. of 0.05% gelatine solution as 'maximum suppressor' for every 50 ml.

In the study of the polarograms of zinc (Fig. 1), the diffusion current of zinc in aqueous solution at 60° (curve 1, Fig. 1) reaches the limiting value at the dropping electrode potential (E_{de}) of −1.10 volts *vs.* S. C. E. Even in solutions containing hydrochloric acid, provided that the p_H is not lower than 2.1, the zinc wave has a clear, though small, ceiling between E_{de} −1.12 and −1.20, and then followed by the hydrogen wave; when the p_H is 2.0 or lower, the hydrogen wave begins to be superimposed upon the zinc wave and there is then no distinct ceiling for the latter (curves 3, 4). At 30° similar curves were obtained but the wave height was smaller due to the decrease of the diffusion current with the decrease in temperature.

The titration arrangement was similar to the one described in a previous paper (Khosla and Gaur, *loc. cit.*). For thermostating, the dropping cell assembly was

clamped on a movable sleeve so that the titration cell could be dipped in or lifted out of the thermostat. 50 Ml. of zinc solutions of different strengths were titrated

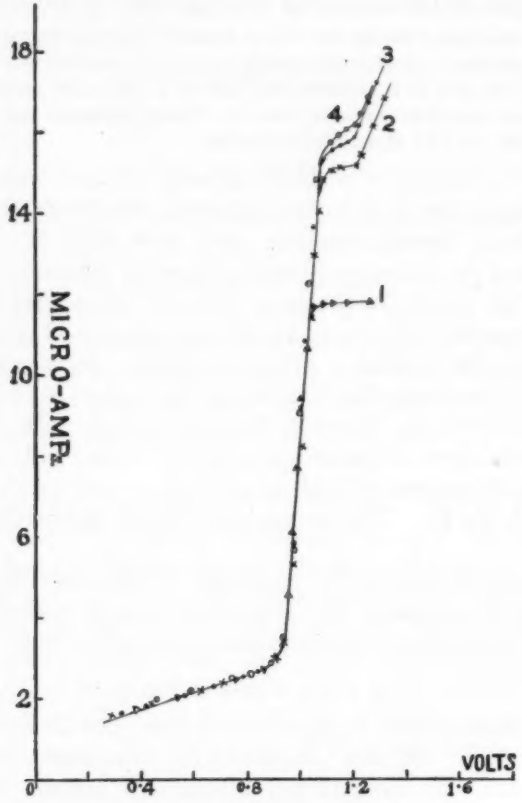

FIG. 1. Polarograms of 1.575 *MM* $ZnSO_4$ in *N*/10–KCl in non-acid (curve 1) and acidic solutions of p_H 21. 2.0, 1.9 (curves 2, 3, 4).

with standard potassium ferrocyanide solution added through a micro-burette graduated to read 0.20 ml. The titrations were carried out at $E_{de} = -1.18$ volts *vs.* S. C. E. when the diffusion current due to zinc had a limiting value in solutions whose p_H was not lower than 2.1. The reaction mixture after each addition of the titrant was thoroughly stirred by bubbling nitrogen and the precipitate was allowed to settle clear of the capillary tip before the diffusion current was measured.

As the titration proceeds, the observed diffusion current due to zinc goes on decreasing linearly with its concentration, and after the equivalence point it attains a constant value corresponding to that of the carrying electrolyte, since potassium ferrocyanide is not reduced at the dropping electrode (Sanigar, *Rec. trav. chim.*, 1925, 44, 549). The observed diffusion current after each addition

of potassium ferrocyanide solution was corrected for the dilution effect by multiplying it by the factor $(V+v)/V$, where 'v' is the total volume of the titrant added up to a given stage, and 'V' is the initial volume of the solution to be titrated. The titre value was obtained from the point of intersection of the two straight portions of the curve. A typical curve depicting the results of titration of 3.15 millimolar solution of zinc with 100.31 millimolar potassium ferrocyanide solution is given in Fig. 2. In the titrations of solutions more concentrated than 1.50 millimolar, it was necessary to precipitate the excess of zinc over 1.50 millimolar concentration with potassium ferrocyanide in the titration vessel before the diffusion current was within the measurable limits of the galvanometer.

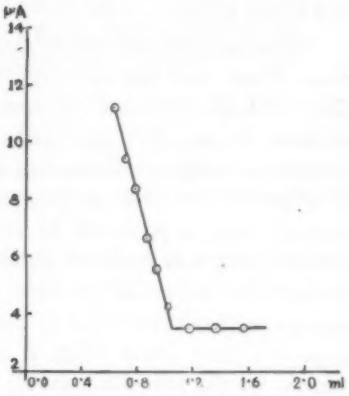

FIG. 2. Amperometric titration curve.

TABLE I

$ZnSO_4$ soln taken=50 ml. of initlal p_H2.1. E_{de}=1.15 volts *vs.* S. C. E.

$ZnSO_4$.	K_4FeCy_6.	Titre values Calc.	Obs.	Diff.	$ZnSO_4$.	K_4FeCy_6.	Titre values Calc.	Obs.	Diff.
(millimolar)		Temp.=30°.			(millimolar)		Temp.=60°.		
1.622	49.75	1.086 ml.	1.05 ml. 1 06	3%	1.622	49.75	1.086 ml.	1.07 ml. 1.06	2%
3.244	49.75	2.172	2.05 2.06	5%	2.433	49.75	1.628	1.59 1.60	2%
4.05	49.75	2.72	2.61 2 62 2.61	4%	3.244	49.75	2.17	2.14 2.15 2.15	1%
3.15	100.31	1.05	1.02 1.02	3%	3.150	100.31	1.05	1.04 1.04	1%
					1.575	100 31	0.525	0.53 0.53	1%
					3.878	103.58	1.24	1.21 1.21	2.4%

The results recorded are tripical of the varuous concertrations tried.

DISCUSSION

The composition of the precipitate formed on the addition of potassium ferrocyanide to the zinc solution is known (de Konick and Prost, *Z. angew. Chem.*, 1896, **9**, 564) to be $K_2Zn_3[FeCy_6]_2$. While performing the titrations in an unacidified medium at 30°, it was observed that the titre values obtained from the amperometric titrations were 8 to 10% lower than those calculated from the known strengths of the reactants, for the formation of $K_2Zn_3[FeCy_6]_2$, and the the p_H of the solution changed from 6.7 at the beginning to 9.25 at the end of the titration. Further addition of potassium ferrocyanide did not appreciably change the p_H of the solution, nor was

any change of p_H value observed by adding a small amount of potassium ferrocyanide to a blank solution of the carrying electrolyte.

The ferrocyanide precipitates are known to suffer hydrolysis in aqueous solutions (Gaur and Bhattacharya, this *Journal*, 1947, 24, 487, 499; 1948, 25, 27, 185, 191, 220; 1950, 27, 251) and the low results of the titration, as well as the observed increase in p_H after the equivalence point, were considered by us to be due to such hydrolysis, which we eliminated in the later titrations by adding increasing amount of hydrochloric acid to the zinc sulphate solutions. The results recorded in Table I were obtained at an initial p_H of 2.1 which increased only slightly after the equivalence point was reached indicating an effective check of the hydrolysis of the precipitate. Solutions of zinc with p_H lower than 2.1 could not be used for the amperometric titrations, as in their case the hydrogen wave began to be superimposed upon the zinc wave (Fig. 1, curves 3, 4), and the ceiling for the limiting diffusion current for the zinc disappeared and the observed diffusion current passing through the cell at any applied value of E_{dc}. could not then be regarded as linearly proportional to the concentration of zinc in the solution. The results of the amperometric titrations at the initial p_H of 2.1 at 30° were still 3 to 5% lower than the calculated titres (Table I). At this temperature the precipitate obtained was rather slow to settle due to its gelatinous nature; therefore, further titrations were performed at 60°, as suggested by kolthoff *et al* (*Ind. Eng. Chem., Anal. Ed.*, 1932, 4, 147). The precipitate then settled about five times as fast as at 30°, and the observed titre values then were only about 2.5% lower than calculated titres (Table I).

At the lower temperature, when the precipitate is gelatinous, zinc ions in contact with it will be adsorbed and probably also occluded by it. At 60° the precipitate obtained is quite granular and then the occlusion and the adsorption of these ions by the precipitate are likely to be less. The higher titre values of potassium ferrocyanide, as observed at 60°, could thus be explained. It also appears probable that due to a higher rate of the reaction at 60°, the equivalence point is more truly reached than at the lower temperature. The titrations made at 45° gave results similar to those at 30°.

Solutions of zinc more concentrated than 3 millimolar were titrated but, as in the case of 3 millimolar solutions, the excess concentration of zinc over 1.5 millimolar had to be precipitated with the titrant before the diffusion current was within the measurable limits of the galvanometer. As the observed titres at higher concentrations of zinc had a tendency to be somewhat low, the solutions of higher concentrations were diluted and then titrated so to avoid excess of the precipitate remaining in contact with the solution and the consequent error due to adsorption.

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MOLECULAR STRUCTURE AND STABILITY OF EMULSIONS OF SOME ALIPHATIC ALCOHOLS AND ESTERS. PART I

By Miss Hemlata J. Kazi and C. M. Desai

Some aliphatic alcohols and their esters have been emulsified by means of potassium oleate by Briggs method. The effect of the nature and length of the aliphatic chain has been discussed in relation to the relative stability of these emulsions determined from the time of their half break, measured from size frequency analysis.

The present communication deals with the emulsification of some aliphatic alcohols and esters to study the effect of the nature and length of the aliphatic chain on emulsion stability.

Experimental

All the emulsions were prepared under comparable conditions by Briggs method (*J. Phys. Chem.*, 1920, **24**, 120), using as the emulsifier potassium oleate-neutral, acid and alkaline. With a view to determining the initial specific area of the disperse phase and its decrease with time, the emulsions were subjected to size frequency analysis (King and Mukherji, *J. Soc. Chem. Ind.*, 1940, **59**, 185). The relative stability of the system was determined by the time required for the interfacial area to diminish to half of its initial value. The data on the interfacial tension of liquids against water and aqueous emulsifier solutions were also obtained by the drop volume method using a micro-syringe (Kazi and Desai, this *Journal*, 1953, **30**, 209, 283). The concentrations of the emulsifier used were 1.25% with *iso*amyl, hexyl and *sec.*-octyl alcohols, 0.62% with *n*-butyl and *iso*butyl alcohols, 1.0% with ethyl malonate and acetaocetate and 3.0% with *iso*propyl, *n*- and *iso*butyl, *iso*amyl acetates, respectively. The phase-volume ratio selected was 43 : 57 in the case of alcohols and 50 : 50 in the case of esters. The above concentrations of the disperse phase and emulsifiers were found to be optimum, because emulsions, prepared otherwise, were found to be very unstable in many cases.

Emulsification.—The disperse phase was added to the dispersion medium (double distilled water) containing a known amount of the emulsifier in a 100 c.c. glass-stoppered cylinder. The mixture was subjected to 50 shakes for half a minute using vertical mode of shaking and then allowed to rest for half a minute ; it was then further shaken likewise for half a minute and again allowed to rest for half a minute. This process was repeated five times and was found to be very effective. In many cases, the emulsions foamed, the amount and stability of the foam being dependent on the nature and concentration of the emulsifier and the disperse phase. The cylinders containing the emulsions were then kept in dark under cardboard cases for size frequency analysis.

Size frequency Analysis.—A magnification of 450 times was used with Leitz Wetzlar microscope of 6L objective and an occular 10X with a tube length of 17 cm. The eye-piece scale was calibrated against stage micrometer, its one division

being equal to 1.4 μ. For actual measurement the usual statistical method was employed.

The cover slips and slides were scrupulously cleaned. For sampling, 0.5 c.c. of the emulsion was taken out by means of a pipette and mixed with 4.0 c.c. of distilled water and 0.5 c.c. of 10% gelatine solution in the case of alcohols. In the case of esters, 0.5 c.c. of the emulsion was mixed with 4.5 c.c. of glycerine, as it was not possible to obtain good results with gelatine. A drop of this mixture was examined under the microscope. The time of half break was obtained by plotting the specific area of interface against time, and then reading the time for the specific area to diminish to half of its initial value. The stability of the emulsions cannot be adjudged by the extent of the specific interface, but its rate of decrease with time is indicative of its stability. Generally, the smaller the rate of decrease of the interface, the greater appears to be the stability. Hence, the time of half break was taken as a measure of emulsion stability.

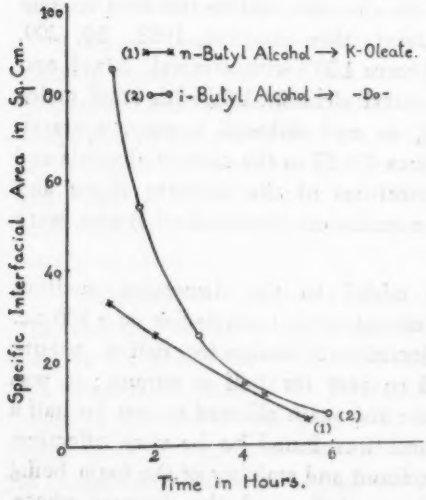

FIG. 1

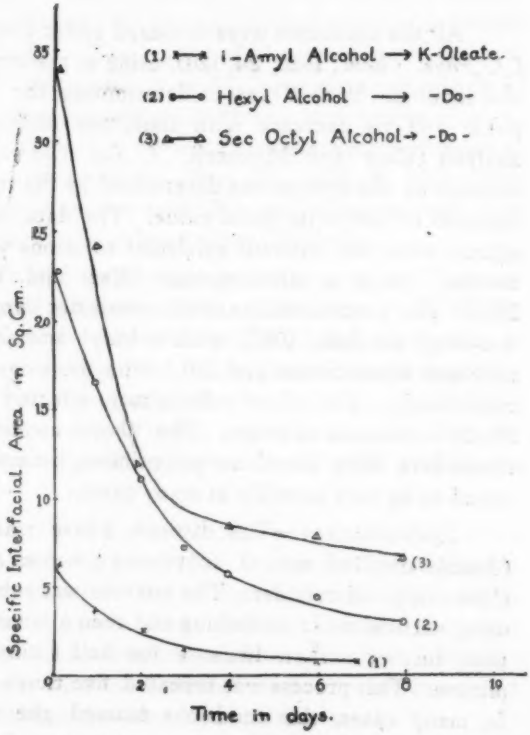

FIG. 2

The graphs in Figs. 1 and 2 and Table I show the decrease of interfacial area with time and Table II shows the time of half break of emulsions with neutral potassium oleate. The general behaviour of emulsions with acid or alkaline soap follows the same pattern.

TABLE I

Specific interfacial area ($\times 10^3$ cm^2) *with* K-*oleate.*

Time in days.	*n*-Butyl acetate						*iso*-Amyl acetate				
	Neutral.	10% Acid.	10% Alkali.	20% Acid.	20% Alkali.	*iso*-Butyl acetate (neutral.)	Neutral.	10% Acid.	10% Alkali.	20% Acid.	20% Alkali.
1	24.536	16.035	19.507	16.512	23.242	42.249	28.649	28.225	24.866	26.375	19.205
2	22.527	15.620	14.632	15.115	20.357	22.470	23.436	12.339	21.204	22.688	14.839
3	21.225	13.503	11.295	14.923	18.326	17.570	18.135	8.415	18.331	16.570	10.030
4	19.769	11.647	10.121	14.605	17.520	...	14.837	4.942	14.061	14.431	7.432
5	18.273	10.800	9.235	12.304	16.635	9.608	11.208	3.358	10.710	11.787	6.067
6	17.342	9.932	8.657	9.512	15.309	...	7.852	2.470	7.015	9.232	4.607
7	15.107	9.579	8.203	7.320	13.434	3.585	5.549	1.309	6.212	7.664	3.729
8	11.913	9.250	7.774	6.620	11.827	...	3.587	1.220	4.773	6.326	3.232
9	9.283	8.714	7.515	5.525	10.749	...	2.257	...	...	4.570	2.843
10	7.194	7.548	7.164	1.875	8.510	...	1.083	...	...	2.800	...
11	6.137	5.400	6.920	...	3.937	...	...	...	4.613	...	1.752
12	5.454	...	6.232	...	...	...	...	...	...	...	...
13	4.912	...	5.722	...	...	...	...	...	...	...	...
14	4.789	...	4.867	...	...	...	0.360	...	3.851	...	0.872

TABLE II

Time of half break with K-*oleate — neutral.*

Liquid.	*n*-BuOH.	*iso*-BuOH.	*iso*-AmOH.	*n*-HexOH.	*sec.* Octyl alcohol.	*n*-Butyl acetate.	*iso*Butyl acetate.	*iso*Amyl acetate.	Ethyl aceto-acetate.	Ethyl malonate.
I. S. T. with water (dynes/cm). ...	3.021	2.406	5.231	8.239	10.60	13.88	13.22	12.12	2.701	13.03
Time of half break ...	2.5 hrs.	3.0 hrs.	1.2 days.	2 days.	1.8 days.	8 days.	2 days.	4 days.	2 hrs.	5 hrs.

DISCUSSION

From the results it appears that it is the rate of decrease rather than the magnitude of the specific interfacial area which characterises the stability of an emulsion. The rate of decrease of area is initially rapid and then becomes slow at later stages due to stabilisation, in case of comparatively stable emulsions. When emulsions, however, break up, there is an abrupt decrease in the area. In the alcohol series, the stability of emulsions appears to change in the following order : *n*-butyl alcohol < *iss*butyl alcohol < *iso*amyl alcohol < hexyl alcohol > *sec.*-octyl alcohol. It

may be inferred that lengthening of the carbon chain tends to impart stability to some extent, but further lengthening tends to diminish it. In the ester series the stability order is as follows: *n*-butyl acetate>*iso*amyl acetate>*iso*butyl acetate>*iso*propyl acetate>ethyl and methyl acetates. The emulsions of ethyl and methyl acetates were found to be extremely unstable, their emulsifying capacity being very weak.

Even though *iso*butyl alcohol and ethyl acetoacetate have extremely low interfacial tensions, their emulsions were found to be very unstable. The reason is that the low interfacial tension facilitates emulsification, but it alone cannot stabilise the emulsified globules. The nature of the interfacial film is the stabilising factor. The nature of the disperse phase and the relative effect of the emusifier thereon determine largely the characteristics of the film. The behaviour of the disperse phase is further determined by its structure and its orientation in space. In case of alcohols, it may be possible that the nature of longer carbon chain may be different from that of shorter chain. The interfacial tension measurements (cf. Kazi and Desai, *loc. cit.*) point to the effect that shorter chains with four or five carbons have more of linear character, while longer chains have more of ring character through H-bond. Comparing the interfacial tensions of *n*-butyl alcohol (3.02 dynes) and *iso*amyl alcohol (5.25 dynes), it is evident that the substitution of methyl group appears to increase the interfacial tension, and at the same time also increase the stability of *iso*amyl alcohol emulsions, when compared to that of butyl alcohol emulsions. Comparison of interfacial tensions of *n*-butyl acetate (13.8 dynes) and *iso*amyl acetate (12.12 dynes) shows that substitution of methyl group for hydrogen lowers the interfacial tension, and also at the same time decreases the stability of *iso*amyl acetate emulsions, when compared to that of *n*-butyl acetate emulsions. The reason for different effects of methyl group substitution may be ascribed to linear nature of alcohols and ring character of esters, as indicated by interfacial tension measurements. Thus, it is apparent that the substitution has a relative effect in space with respect to the structure of the molecule. With the change in the orientation of the molecular structure, it is probable that the change in the substitutent effect also takes place. The work of Kamath and Vaidya (unpublished) has indicated that the methyl substitution in benzene and aniline tends to increase emulsion stability. Besides this, the length of the carbon chain also plays an important role, because *iso*butyl alcohol and acetate emulsions are less stable than those of *iso*amyl alcohol and acetate, respectively, as the length of the aliphatic chain in the former is shorter than in the latter cases. Further work in this direction is in progress.

The authors are indebted to Dr. B. K. Vaidya, Assistant Director, Ahmedabad Textile Industrial Research Association, for his suggestions and interest and also express their gratitude to the college authority for the grant to meet the expense in the work.

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STUDIES IN METAL TELLURATES : DETERMINATION OF BISMUTH AS BISMUTH TELLURATE

By G. S. Deshmukh and E. T. Varkey

Results are given for the gravimetric determination of bismuth as bismuth tellurate. It is shown that the compound obtained under the given operative conditions has the formula $(BiO)_2TeO_4.2H_2O$.

The formation of tellurates, especially of the heavy metals, by the addition of alkali salts of telluric acid or by fusion has been investigated by numerous workers (Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", 1931, Vol. 11, pp. 88-97). Preliminary experiments in these laboratories showed that under certain operative conditions the addition of an alkali tellurate to an almost neutral or slightly acidic solution of bismuth salt gave an amorphous precipitate of bismuth tellurate. These observations led to a systematic study of this precipitation process with a view to utilising the data for the quantitative determination of bismuth.

Experimental

An aqueous solution of sodium tellurate of B. D. H. reagent grade quality was used for the precipitation of bismuth. The tellurium content of this sodium salt, found by Gutbier and Huber's method (*Z. anal. Chem.*, 1914, 53, 430), showed that the sample was practically free from impurities. An almost neutral or slightly acidic solution of bismuth was prepared by digesting a weighed quantity of Merck's sodium bismuthate in dilute nitric acid and removing the acid by repeated evaporation of the solution on a water-bath. Dilute ammonia was now added till a slight permanent turbidity appeared. This was dissolved in just sufficient quantity of dilute nitric acid. The bismuth content of this solution was determined by the pyrogallol method (Vogel, "A Text Book of Quantitative Inorganic Analysis", Longman Green and Co., 1945, p. 507). An aliquot portion of the solution was heated to about 70°, and the sodium tellurate solution was run in slowly with constant stirring till the precipitation was complete. The contents were boiled for two minutes and the precipitate was allowed to stand overnight. It was then filtered through a weighed sintered glass crucible and washed by decantation with hot water. Finally the precipitate was transferred to the crucible and washed several times with small portions of warm water till free from excess of tellurate. The crucible was dried in an air-oven at 120°-130°, for about an hour, cooled and weighed. From the weight of the precipitate, thus obtained, the amount of bismuth in a given quantity of the original solution taken for precipitation was calculated by assuming the formula of the bismuthyl tellurate as $(BiO)_2TeO_4.2H_2O$. The results are shown in Table I.

TABLE I

Bi (by pyrogallol method).	Wt. of ppt. $(BiO)_2TeO_4.2H_2O$.	Bi calc. from the wt. of ppt.	Diff.
0.0508 g.	0.0819 g.	0.05053 g.	0.00027 g.
0.0677	0.1094	0.0675	0.0002
0.0847	0.1368	0.08439	0.00031
0.1015	0.1637	0.1009	0.0006
0.1353	0.2183	0.1347	0.0006
0.1692	0.2763	0.1688	0.0004
0.2030	0.3270	0.2017	0.0013
0.2370	0.3830	0.2362	0.0008
0.2713	0.4364	0.2693	0.0020

It is seen that the amount of bismuth, calculated on the basis of the formation of $(BiO)_2TeO_4$, $2H_2O$ by the above procedure, agrees within limits of experimental error with that obtained by the standard pyrogallol method. As an alternative check for the accuracy of these results, the possibility of estimating tellurium in the excess sodium tellurate added for precipitation of bismuth is now being investigated.

The authors' thanks are due to Professor S. S. Joshi for facilities and kind interest in the work.

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STUDIES ON GUM JEOL (*LANNEA GRANDIS*, ENGLER). PART IX. INTERACTION OF JEOLIC ACID WITH NON-ELECTROLYTES

By S. N. Mukherjee and S. K. Sinha

Protophilic non-electrolytes like acetone and ethyl alcohol interact with jeolic acid with effects roughly similar to those with neutral salts. Both hydrogen-ion activity (a_H) and total titratable acidity (c_H) show tendencies to increase with increasing addition of these non-electrolytes, the latter reaching maximum values at higher concentrations. The maximum reached with acetone is, however, higher than that with ethyl alcohol.

Non-electrolytes are known to have a marked influence on electrochemical properties of substances in general. Many of them have a low dielectric constant compared to that of water, as a result of which electrostatic interactions between ions assume a considerable magnitude. Hence, all electrochemical properties having their origin from ionic interactions will be more or less intensified by such a lowering of dielectric constant. In this paper this point has been specially examined with two non-electrolytes : acetone and ethyl alcohol. Properties studied refer only to the changes in free acidity (a_H) and total acidity (c_H). The effect of neutral salts on total acidity was also examined and the results obtained have been taken into consideration in elucidating the observed behaviour of non-electrolytes.

Experimental

The non-electrolytes used here were ethyl alcohol and acetone, both of which were of 'guaranteed reagent' quality of E. Merck. The salts used were KCl, NaCl, $BaCl_2$ and $CaCl_2$, all of 'pro analysi' quality. Solutions were prepared in equilibrium water of specific conductance $1.3+10^{-6}$ mho at 35°. The jeolic acid solution had a concentration of 1% in the final stage.

Variations of free and total acidities (a_H and c_H respectively) with different concentrations of these electrolytes and non-electrolytes were observed by keeping the concentration of the jeolic acid solution constant (namely 1%). For this reason 5 c.c. of a 2% solution of jeolic acid were mixed with 5 c. c. of a mixture of water and the electrolyte or non-electrolyte solution (as the case be) in varying proportions so that the final concentration of the acid solution was exactly 1%.

Discussion

Influence of Neutral Salt on Total Acidity.—Total titratable acidity of the jeolic acid in presence of the salts mentioned above was determined by potentiometric titration of the acid with the corresponding base ; for example, when the effect of KCl was to be studied the base used for titration was KOH, and so on. Actual titration curves have not been shown here as they present nothing new beyond

what has been mentioned in the previous communication on the interaction of jeolic acid with bases (this *Journal*, 1953, 30, 201). Results obtained here are shown in Table I.

TABLE I

Temp. – 35 ± 0.1°.

Conc. of salt.	Total acidity (in m. equiv. of base/100 g. acid.				Cationic order.
	NaCl.	KCl.	$BaCl_2$.	$CaCl_2$.	
0 *N*	89	65	104	112	Ca>Ba>Na>K
0.1	92	62	100	109	"
0.2	95	66	110	115	"
0.3	—	67	112	117	Ca>Ba>K
0.4	—	69	122	118	Ba>Ca>K
0.5	—	73	127	121	"

The concentrations of the salts refer to the final concentrations attained after being mixed with the acid solution. It will be evident that the total titratable acidity of the jeolic acid increases slightly with increasing addition of the neutral salts, and the amounts of salts necessary to bring about such small increments in total acidity are quite high. At zero concentration of the salts the total acidity in fact refers to those observed with different bases and shows a cationic order of Ca› Ba› Na› K as reported earlier (*loc. cit.*). The p_H of the inflexion points has been observed to be the same in all cases, viz., about 7.2.

It appears from this that some of hydrogen ions are firmly bound to the micelles, and they do not come out easily when during titration the equilibrium is distrurbed by removal of hydrogen ions from the bulk of the solution by neutralisation. If this were so then all bases would have yielded the same total acidity. Another interesting feature to be noted is that the liberation of hydrogen ions by different cations, (or the base exchange), takes place to different degrees depending on the nature and concentration of the cations. It begins at low concentrations of the salts, and is not complete even at a concentration as high as 0.5*N*, although the rate of exchange is much reduced at higher concentrations. It appears that a continued treatment with salts, viz., a lengthy leaching process, may ultimately remove all these hydrogen ions.

Comparing the effects of $BaCl_2$ and $CaCl_2$, the latter is found to produce a higher total acidity than the former at corresponding concentrations. But above a concentration of 0.3*N*, the order is reversed. This is quite parallel to the order in which the two salts lower the p_H of the jeolic acid solution, as reported earlier (*loc. cit.*).

This parallelism between the increase in total acidity and a corresponding derease in p_H of the jeolic acid solution obviously suggests that the change in total acidity is an effect of base exchange and the greater the base exchange capacity of a cation, the higher is the total acidity produced.

Influence of Non-electrolytes on Free and Total Acidity: (*i*) *Free Acidity.*— The influence of increasing concentrations of acetone and ethyl on the p_H of jeolic acid solution was investigated with the results appearing in Table II.

TABLE II

Jeolic acid solution = 1%.

Conc. of acetone. (Vol.)	p_H.	$a_H \times 10^4 N$.	Conc. of EtOH (Vol.)	p_H.	$a_H \times 10^4 N$.
0%	4.90	1.00	0%	4.0	1.00
10	3.80	1.59	10	3.9	1.26
20	3.80	1.59	20	4.0	1.00
30	3.72	1.91	30	3.9	1.26
40	3.70	1.99	40	3.85	1.41
50	3.65	2.24	50	4.05	0.89

Evidently there is a regular decrease of p_H with increase in the concentration of acetone. With ethyl alcohol variations in p_H are not only less marked but they are also irregular.

(*ii*) *Total Acidity.*—Jeolic acid solution (1%) was titrated potentiometrically with NaOH in presence of acetone and ethyl alcohol respectively. Total acidities are shown in Table III.

TABLE III

Acetone (by vol.).	Total acidity in m.e. of base per 100 g. of acid.	Alcohol (by vol.).	Total acidity in m. e. of base per 100 g. of acid.
0%	89.0	0%	89.0
20	106.8	20	91.5
30	117.0	30	86.5
40	150.0	40	96.5
50	150.0	50	96.5

Thus the total acidity is found to increase with increasing concentrations of both acetone and alcohol. With acetone, the variations are regular, but with alcohol, a slight irregularity is obvious. There is thus a rough parallelism between the

changes in the free and total acidities in this case again (vide columns 3 and 6 of Table II and columns 2 and 4 in Table III).

Another interesting feature with acetone is that there appears a maximum value of total acidity at 150 m.e. of the base per 100 g. of the acid at a concentration of 40% by volume of acetone. This is more than 3/2 times of that obtained in absence of acetone and is much higher than the values obtained by addition of quite high concentrations of neutral salts. Besides, the rate of change of total acidity with the concentration of acetone is much higher than that with alcohol.

In this connection it is interesting to note that acetone has been observed to be a better precipitant of jeolic acid from its aqueous solution than ethyl alcohol which precipitates the acid at as high a concentration as 85% by volume.

Thus, with acetone at least, both free and total acidities of the jeolic acid increase with increasing acetone concentration and the changes are more pronounced than those produced by interaction with neutral salts (*vide supra*). The change in free acidity cannot be explained by looking upon it as an effect of the altered interionic attractions consequent upon the drastic changes in the dielectric constant of the medium, because such changes in the dielectric constant would affect the activity of hydrogen ion in the opposite direction in the light of the relation,

$$-\ln f = \frac{AZ^2\sqrt{2\mu}}{(DT)^{1.5}}$$

where f stands for the activity coefficient of hydrogen ions, μ, for the ionic strength of the solution, Z for the valency of the ion (-1 for H^+) and D and T have their usual significance. The effect of addition of acetone appears to be the introduction of more hydrogen ions into the bulk of the solution besides altering their activity. This is corroborated by corresponding changes in the total acidities, because unless fresh hydrogen ions come into the bulk of the solution from some source, it is difficult to visualise how the total acidities can change. In this respect the behaviour of acetone is parallel to that of the neutral salts, the effects being more intense in this case.

With increase in the concentration of acetone, there is another probability which should not be overlooked. The solution of jeolic acid behaves as a hydrophilic colloid, and each micelle is surrounded by a hydrosphere. Addition of acetone in increasing amounts would tend to replace some of the water molecules surrounding the micelle (compare the higher dipole moment of acetone $=2.9\times10^{-18}$ against that of water equal to 1.8×10^{-18}; *Trans. Faraday Soc.*, 1934, **30**, appendix). When some of the molecules of water are thus replaced, the dielectric constant of this sphere would be considerably reduced and ions in the double layer would be under more intense electrostatic force. This will serve to increase the attractive force on the bound hydrogen ions. It is thus easy to understand that the maximum of total acidity in presence of non-electrolytes may be due to two reasons. Either all the hydrogen ions bound in the double layer have been removed into the bulk

of the solution by the non-electrolyte or only a part of it has been removed, the rest being more strongly held by the intensified electrostatic attractions, and a maximum of total acidity is reached. In the latter case, different non-electrolytes will be expected to show different maxima of total acidity, and this is, in a way, borne out by the fact that the maximum with ethyl alcohol is different from that of acetone (vide Table III).

Conclusion

Thus the properties of jeolic acid, as reported in this communication and the previous one (*loc. cit.*), show that

(*i*) The jeolic acid in aqueous solution shows the property of base exchange in its interaction with bases, acids and neutral salts and this effect depends on the nature and valency of the cations concerned. Both free and total acidities increase in presence of the neutral salts.

(*ii*) Non-electrolytes of protophilic nature can also affect the free and total acidity in a like manner. The increase of hydrogen-ion activity at the same ionic strength can find no other explanation but a possible arrival of hydrogen ions from some source. The interionic attraction theory alone has been shown to be insufficient to explain the nature and extent of this effect.

From these facts it is suggested that the behaviour of jeolic acid in aqueous solution cannot be wholly explained by the interionic attraction theory regarding the acid as a simple electrolyte. On the contrary, if we imagine that the non-ionised acid molecules first aggregate into micelles which then ionise and form charged colloidal particles exhibiting electrophoresis, the behaviour becomes easy to understand. The charged micelles then become covered with an electrical double layer as in ordinary colloidal systems and the counter-ions (hydrogen ions in this case) are liable to be exchanged or removed in the same manner as in other colloids showing base exchange and related phenomena. The effects in this case are, however, much less pronounced than in some well known colloidal acids like hydrogen clays, hydrogen bentonite, silicic acid, etc., but the nature of the properties observed is the same.

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INTERACTION OF BROMINE AND METHYLAMINES

By R. H. Sahasrabudhey, M. A. Prasad Rao and (Miss) Indumati Bokil

When bromine reacts with solutions of methyl- and dimethylamines in an indifferent solvent medium like benzene or ether, a mono N-bromo derivative is formed in solution and concomitantly the amine hydrobromide is precipitated, which combines with additional bromine, if present, to form perbromide (s). In the case of trimethylamine a lemon-yellow dibromo addition product is precipitated, both the bromines of which are reactive to potassium iodide. From its behaviour, it appears to be a typical N-bromo compound and not bromotrimethylammonium bromide, as suggested by Hantzsch and Graf. The perbromides are unstable in presence of moisture and strong alkali, but in presence of cold dilute alkali, they give rise to corresponding N-bromoamines. The various properties and interrelationships of these compounds have been indicated.

Although N-dibromomethylamine had been reported to be formed by the action of hypobromite on aqueous methylamine (Hofmann, *Ber.*, 1883, **16**, 558), Remsen and Norris came to the conclusion that methylamine did not give either a N-bromo derivative or a perbromide (*Amer. Chem. J.*, 1896, **18**, 90). We have now found that when bromine and methylamine react in cold dry benzene or ether, N-monobromomethylamine (I) is formed in solution and simultaneously, methylamine hydrobromide is precipitated which, if excess of bromine is present, forms a perbromide (II). The reaction can be represented as :

$$(i)\quad 2MeNH_2 + Br_2 \longrightarrow \underset{(I)}{MeNHBr} + MeNH_2, HBr$$

$$(ii)\quad 2MeNH_2, HBr + Br_2 \longrightarrow \underset{(II)}{2MeNH_3Br_2}$$

In the case of dimethylamine the reaction proceeds along the same lines as indicated for monomethylamine, and the following products are obtained depending on the amount of bromine used :

Me_2NBr	$Me_2NH_2Br_2$	$Me_2NH_2Br_3$
(III)	(IV)	(V)

The compound (III) is identical with the that obtained by the action of hypohalite (Willstättar and Hottenroth, *Ber.*, 1904, **37**, 1775) and that formed by the action of dilute alkali on the perbromide (Norris, *Amer. Chem. J.*, 1898, **20**, 51).

The perbromide (IV) is identical with Norris' compound (*loc. cit.*) ; the compound (V) does not appear to have been reported earlier. The compounds (IV) and (V) are mutually interconvertible and the former is the stabler variety. Their behaviour towards water is similar (vide Experimental) to that of (II) and that towards alkali can be represented as :

$$(a)\quad Me_2NH_2Br_2 + NaOH \xrightarrow{\text{cold, dilute}} Me_2NH + NaBr + NaOBr$$

$$(b)\quad Me_2NH + NaOBr \rightleftarrows Me_2NBr + NaOH$$

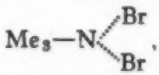
The compound (III) on treatment with dry HBr in benzene does not give a hydrobromide but liberates free bromine. This is reminiscent of the behaviour of N-bromoacetanilide :

$$Me_2NBr + HBr \longrightarrow Me_2NH + Br_2.$$

Trimethylamine in benzene and ether forms the same dibromo addition product Me_3NBr_2 (VI), as reported by Hantzsch and Graf (*Ber.*, 1905, **38**, 2157) but its hydrobromide in water yields a red viscous liquid which is most probably a higher perbromide or a solution of the perbromide in excess of bromine. On standing it gave Me_3NHBr_2 (VII)

The dibromide (VI) with excess of bromine added a further atom of the latter and gave the tribromide Me_3NBr_3 (VIII) which on standing lost an atom of bromine to reform the dibromide (VI), the stabler of the two. In presence of moisture both (VI) and (VIII) gave (VII),

The perbromide (VII) like other perbromides, when treated with dilute alkali, affords the dibromide (VI) which from its mode of formation and properties appears to be more akin to a N-bromo compound than a salt like $(Me_3NBr)^+Br^-$. Its structure probably can be better represented as



where both the bromines are held by singlet links.

EXPERIMENTAL

N-Bromomethylamine.—When a cold dry solution of methylamine in benzene or ether was treated with a half molar equivalent of bromine in the same solvent, a colorless precipitate of methylamine hydrobromide (m.p. 250°) was immediately thrown down, and in the solution was formed the N-monobromomethylamine which could be separated by fractional distillation. It is an orange-yellow liquid, b. p. 47°-48°, insoluble in water with a characteristic pungent odour. It liberated iodine from acidic potassium iodide but in a neutral medium gave a maroon-red compound (Berg, *Compt. rend.*, 1893, **116**, 887).

Methylamine Perbromide.—When methylamine hydrobromide was treated with a solution of bromine in benzene, bromine was 'absorbed' by the former. The red solid so obtained was very unstable and parted with its bromine in contact with moisture or on mere pressing between folds of filter papers. The following experiments clearly indicate that this is a definite compound and not a case of mere physical adsorption :

Known quantities of pure dry methylamine hydrobromide were taken in several test tubes and bromine in benzene was added in different molar ratios, keeping the final volumes constant. The contents were allowed to stand with occasional shaking for different durations of time and in some cases cooled (5°). The supernatant benzene layer was then thoroughly drained and bromine, reactive

towards KI, was estimated in the red solid residue. Results agreed with the calculated values for the perbromide : (Found : Br, 0.1380, 0.1390, 0.1390. Calc. for $[MeNH_3]Br_2$: Br, 0.1326, 0.1480, 0.1358 g.).

N-*Bromodimethylamine and Dimethylamine Perbromides.*—When bromine and dimethylamine were treated as in the above experiment, a crystalline yellow perbromide (m.p. 91°), identical with the perbromide reported by Norris (*loc. cit.*) was obtained, and in the solution was formed $Me_2N.Br$ which could be conveniently fractionated out from an ethereal solution, b.p. 66-68°. This is identical with the compound obtained by Willstätter and Hottenroth (*loc. cit.*). When excess of bromine was used another crystalline red product was obtained, m.p. 74°. [Found : Br (active towards KI), 54.6, 55.7 ; Br (total), 82.6, 82.2. Calc for $Me_2NH_2Br_3$: Br (active), 55.9 ; Br (total), 83.9 per cent]. On standing it loses an atom of bromine and gives the lower perbromide of m.p. 91°.

Both the perbromides on reduction with bisulphite or treatment with strong alkali give dimethylamine. They decompose in presence of water into Me_2NH,HBr, and bromine. With dilute alkali they form N-bromodimethylamine, b.p. 66-68°. These perbromides can also be obtained directly by the action of bromine on Me_2NH,HBr suspended in benzene.

Trimethylamine Dibromide, Tribromide and Perbromide.—When a solution of trimethylamine in ether was treated with bromine, a pale yellow dibromo addition product, Me_3NBr_2, m.p. 76°, was obtained. With excess of bromine a red tribromide, m.p. 65-66° (decomp.) was obtained. [Found : Br (total),79.8, 79.95 ; Br (active), 79.9. Me_3NBr_3 requires Br, 80.27 per cent]. The di- and tribromides are decomposed by strong alkali, acids and water.

An aqueous solution of trimethylamine hydrobromide on treatment with excess of bromine in dilute alkali also gave the tribromide. But if bromine was added to trimethylamine hydrobromide suspended in benzene, a red viscous liquid was formed (Norris, *loc. cit.*) which on standing deposited orange red-needles, m.p. 105° (decomp.). [Found : Br (total), 73.5 ; Br (active), 36.4, 36.57. $(CH_3)_3NHBr_2$ requires Br (total), 72.7 ; Br (active), 36.35 per cent]. This is evidently a perbromide. On the other hand, if the above red liquid was treated with dilute alkali, it formed the tribromide (*vide supra*), m.p. 65-66° (decomp.). The pure perbromide Me_3NHBr_2, when similarly treated, gave the dibromide Me_3NBr_2, m.p. 76° (decomp.). These reactions clearly indicate that the di- and tribromide are most probably N-bromo compounds ; they are not perbromides.

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STUDIES IN THE SYNTHESIS OF 4-HYDROXYQUINOLINE USING ACETIC ANHYDRIDE AND SULPHURIC ACID. PART I

By B. P. Bangdiwala and C. M. Desai

Ethyl β-arylaminocrotonates have been cyclised using acetic anhydride and sulphuric acid, affording 4-hydroxy-2-methylquinoline and its derivatives in good yields. Ethyl β-*meta*-substituted anilinocrotonates give only the 5-isomer. Oxalates and 4-chloro derivatives of a few of these compounds have been prepared.

The method of Conrad and Limpach (*Ber.*, 1887, **20**, 947; 1931, **64**, 969) has been used to obtain 4-hydroxyquinoline derivatives from β-arylamino-α : β-unsaturated esters. Modifications resulting in increased yields have been made by the use of a number of high boiling solvents (Ashley, *Proc. Roy. Soc.*, 1933, **B113**, 295; Price and Roberts, *J. Amer. Chem. Soc.*, 1946, **68**, 1204).

Cyclisation of the crotonates has now been observed to take place with good yields by the use of acetic anhydride and sulphuric acid at room temperature, as heat of the reaction alone is sufficient for the purpose. The crotonates were prepared by the method of Coffey, Thomson and Wilson (*J. Chem. Soc.*, 1936, 858). In the present method, ethyl β-*m*-toluidino- and *m*-chloroanilino-crotonates gave only the 5-isomer (Bangdiwala and Desai, *Curr. Sci.*, 1952, **21**, 256). Using the same method, 4-hydroxyquinolines have been obtained from ethyl β-anilinio-, β-*o*-(and *p*)-toluidino, β-*o*- (and *p*) -anisidino,-β-*p*-phenetidino-, β-1 : 3 : 4- and 1 : 4 : 5-xylidino-, β-*p*-chloroanilino- and β-α-naphthylamino-crotonates. Out of these, 4-hydroxy-2 : 5 : 8-trimethylquinoline is new. Lockhart and Turner (*J. Chem. Soc.*, 1937, 420) had prepared 4-hydroxy-2-methyl-6-ethoxyquinoline, but did not mention the yield and m.p. of the product. 4-Hydroxy-2-methyl-5-chloroquinoline also has been isolated for the first time.

Experimental

4-Hydroxy-2 : 5-dimethylquinoline.—To a mixture of acetic anhydride (20 c. c.) and ethyl β-*m*-toluidinocrotonate (10 g.) H_2SO_4 (conc.) was gradually added when considerable heat was developed. After keeping the mixture for 15 minutes at room temperature, it was poured on ice and neutralised with NaOH. The solution was heated with charcoal and filtered hot. The filtrate was cooled, then just acidified, and the product (5.6 g., m. p. 264-68°) was twice crystallised from aqueous alcohol, m. p. 274°. (shrinks at 273°); mixed m. p. with an authentic specimen prepared by the methed of Spivey and Curd (*J. Chem. Soc.*, 1949, 2656), remained undepressed. Spivey and Curd (*loc. cit.*) give m.p. 278°, while Backeberg and Friedmann (*J. Chem. Soc.*, 1938, 975) give m.p. 273°.

Its oxalate was prepared by adding a boiling alcoholic solution of oxalic acid (1.1 g.) to alcoholic solution of the product (2.9 g.). The solution was allowed to cool to 60° and maintained at this temperature for 10 minutes, when the oxalate separated (3.1 g.), m.p. 210°. The product was crystallised from alcohol, m. p. 212-13° (Found : N, 6.6. $C_{11}H_{11}NO$, $\frac{1}{2}H_2C_2O_4$ requires N, 6.4 per cent). The pure oxalate was decomposed with 25% sodium hydroxide and the resulting hydroxyquinoline was crystallised from alcohol, m.p. 274°.

4-Chloro-2 : 5-dimethylquinoline.—The above quinoline (2 g.) was refluxed with $POCl_3$ (10 c. c.) for 20 minutes, cooled and then poured on ice. The solution was then basified with strong NaOH solution, when a voluminous mass of the 4-chloro compound separated (1.6 g.). The product was crystallised from alcohol, m.p. 73°. (Found : N, 6.9 ; Cl, 18.8. $C_{11}H_{10}NCl$ requires N, 7.3 ; Cl, 18.5 per cent).

4-Hydroxy-2-methyl-5-chloroquinoline.—Acetic anhydride (20 c.c.) was added to ethyl *β-m*-chloroanilinocrotonate (10 g.). followed by a slow addition of H_2SO_4 (conc., 15 c.c.). The product was worked up as before (3.2 g., m.p. 253-56°). It was further crystallised from aqueous alcohol, m.p. 261-62°, with previous shrinking at 259°. M.p. of the 7-isomer is 312°. (Found : N, 7.0 ; Cl, 18.1. $C_{10}H_8ONCl$ requires N, 7.2 ; Cl, 18.3 per cent).

Its oxalate was prepared as before. The m.p. of the oxalate was found to be 221°, if the bath was kept previously heated at 219-20° ; but if it was slowly heated, shrinking and blackening commenced at 210° and m.p. was not definite. (Found : N, 6.1 ; Cl, 14.6. $C_{10}H_8ONCl$, $\frac{1}{2}H_2C_2O_4$ requires N, 5.9 : Cl, 14-8 per cent).

2-Methyl-4 : 5-dichloroquinoline.—4-Hydroxy-2-methyl-5-chloroquinoline (4 g.) was refluxed with $POCl_3$ (20 c.c.) and the product worked up as before, m.p. 76° ; Spivey and Curd, (*loc. cit.*,) give m.p. 89° for the product prepared by a different method. (Found : N, 6.4 ; Cl, 33.8. Calc. for $C_{10}H_7NCl_2$: N, 6.6 ; Cl, 33.5 per cent).

In the same way 4-chloro-2-methyl-6-ethoxyquinoline (m.p. 64°, yield 74%) and 4-chloro-2-methyl-6-methoxyquinoline (m.p. 98°, yield 66%) were prepared from their corresponding 4-hydroxy compounds. In the case of the latter compound, Basu and Chandran (*J. Sci. Ind. Res.*, 1950, 8, 228) give m.p. 92°, while Conrad and Limpach (*loc. cit.*) give m.p. 100°.

Other 4-hydroxyquinolines were prepared as before. The m.p.s and yields of various 4-hydroxy-2-methylquinolines are shown in Table I

TABLE I

Compounds.	M.p.	Yields	Compounds.	M.p.	Yield
1. Unsubstituted	230°	66%	7. 6-Ethoxy	263-64°	64%
2. 8-Methyl	263-64°	60	8. 6 : 8-Dimethyl	273°	52
3. 5-Methyl	274°	73	9. 5 : 8-Dimethyl	248°	53
4. 6-Methyl	278-79°	58	10. 5-Chloro	261-62°	40
5. 8-Methoxy	229-30°	62	11. 6-Chloro	321-22°	57
6. 6-Methoxy	300°	58	12. 7 : 8-Benzo	340° (decomp.)	38

Further work on similar lines with other *β*-ketonic esters is in progress.

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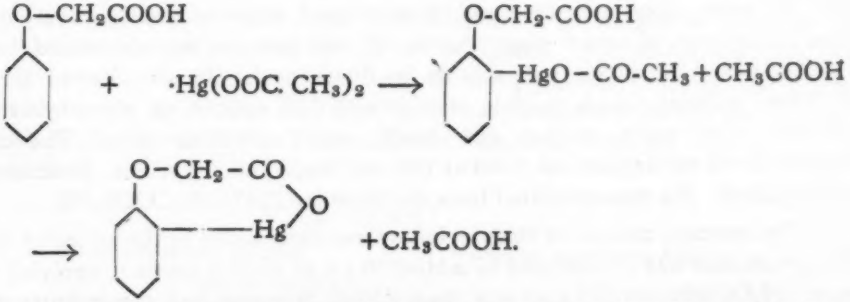
THE ESTIMATION OF MERCURY: ACTION OF PHENOXY-ACETIC ACID ON SALTS OF MERCURY

By Sachindra Kumar Datta

Mercury can be estimated with phenoxyacetic acid from mercurous nitrate, perchlorate and mercuric nitrate and perchlorate solutions, by direct weighing of the salt. Mercury can also be separated from silver anl lead, and can be estimated in their presence, with the help of this reagent.

It has been observed by Guha Sircar and Datta (this *Journal*, 1950, **27**, 358) that mercuric acetate or mercuric oxide in acetic acid gives an almost quantitative yield of organo-mercury derivatives with many aryloxy fatty acids, when heated at 100° for about 3 hours. The possibility of using phenoxyacetic acid in the estimation of mercury has led the author to an extensive investigation on the action of this reagent on various salts of mercury. Phenoxyacetic acid has been seen to produce true organo-metallic derivatives of the type R-Hg-X, where mercury enters the benzene nucleus, and is firmly held, as the compound is stable to acids and alkalies. Such mercuration of phenoxyacetic acids cannot be effected by $HgCl_2$ or $Hg(CN)_2$, nor do they form any simple salts of mercury with phenoxy-acetic acid. But mercurous nitrate, perchlorate and mercuric nitrate and perchlorate give immediate and voluminous precipitates with the reagent, forming only its mercury salts, and not true organo-metallics, as they are decomposed easily with dilute alkalies to the oxides of mercury. The non-formation of any salt of this acid with $HgCl_2$ or $Hg(CN)_2$ can be explained by pointing out that the chloride and the cyanide of mercury are but very slightly ionised in solution and the non-formation of any true organo-metallic compound with the help of $HgCl_2$ or $Hg(CN)_2$, may be visualised, if we assume the following series of reactions in the formation of the organo-mercurial, anhydride of hydroxymercuri-phenoxyacetic acid ;



with the help of mercuric acetate though the acetoxy compound could not be isolated. But $HgCl_2$ cannot react in the above manner (cf. Whitmore, "Organic Compounds of Mercury", 1921)

Due to the ease in the ionisation, in the case of the other salts of mercury, mercury salts of phenoxyacetic acid are formed readily, without producing any true organo-mercurial. The interesting fact, that the precipitates of the above kinds are quantitative, has led the author to examine the use of this reagent in the estimation

of Hg (ous and ic), excepting the chlorides and cyanides. Mercury can also be separated from Pb and Ag present in the form of nitrates in mercury salt solutions, with the help of this reagent. These metals do not interfere with the precipitation of mercury. Exact and rapid methods for the estimation of mercury is still lacking. Though the method described in this communication is not applicable to all salts of mercury, it may advantageously be used for the nitrates and perchlorates of mercury. Mercurous nitrate is estimated by KBr solution volumetrically with bromophenol blue, as an indicator, but the end-point is very difficult to fix due to the presence of mercurous bromide precipitate in the titrant. The method under description may be succesfully applied as mercury can be determined by direct weighing after drying the precipitate at about 100° and finally in a vacuum desiccator. Mercury can also be estimated by the sulphide or other methods, after the decomposition of the organo-mercury salts.

EXPERIMENTAL

Estimation of Mercury in Mercuric Nitrate and Perchlorate Solutions.—Phenoxyacetic acid was prepared from phenol and chloroacetic acid (*J. Amer. Chem. Soc.*, 1931, 53, 304 ; 1943, 65 1555 ; Datta and Guha Sircar, *loc. cit.*). A stock solution of mercuric nitrate (Merk) of approx. 0.1*N* strength containing a little nitric acid was prepared, and also a 0.1*N* solution of mercuric perchlorate by dissolving yellow oxide of mercury (A.R) in perchloric acid (Mathers and Germann, *J. Chem. Soc.*, 1911, 100, 577) The mercury contents of these solutions were determined by precipitation as sulphides (Caley and Burford, *Ind. Eng. Chem. Anal. Ed.*, 1936, 8, 43).

An aliquot quantity of these mercuric salt solutions was taken in a breaker and was diluted to 50 c.c. with water. A cold 0.5% solution of phenoxyacetic acid in water was added dropwise in the cold, with constant stirring, till complete precipitation. A white silky crystalline precipitate formed, which settled down very quickly. Good results were obtained when the p_H of the solution was maintained between 2 and 3, as the precipitate was soluble in dilute acids. It was filtered through a previously weighed Gooch crucible, washed with 0.1% solution of phenoxyacetic acid and then with water, alcohol and finally with anhydrous ether. The crucible containing the precipitate was dried at 100° and finally in a vacuum desiccator, and then weighed. Hg was calculated from the formula $(PhO.CH_2.COO)_2Hg$.

The mercury content of the precipitate was determined by the following method. The precipitate was decomposed by adding 10 c.c. of H_2SO_4 (conc.), applying gentle heat. H_2O_2 solution (3-5 c.c.) was then added dropwise and the mixture shaken. On the reaction being subsided, the mixture was heated over a low flame for about 20 minutes and 5 c.c. more of H_2O_2 were added. Heating was continued till all organic matter was destroyed, which was indicated by the formation of a clear solution. The solution was cooled and diluted to about 200 c.c., and the excess of H_2O_2 was removed by titrating with 0.1*N*-$KMnO_4$ solution. Then mercury was precipitated with H_2S, filtered through a weighed Gooch crucible and dried at 105°-110°. The dry precipitate was extracted with CS_2 to remove any precipitated sulphur ; again, it was

dried to a constant weight. From the weight of HgS the amount of mercury was calculated. [Found : Hg, 39.80. $(C_6H_5\text{-}O\text{-}CH_2\ COO)_2Hg$, requires Hg. 39.84 per cent]. The results have been collected in Table I.

TABLE I

Mercuric nitrate solution.				Mercuric perchlorate solution.			
		Mercury found by				Mercury found by	
Hg present in soln.	Mercuric salt.	Direct weighing.	Decomposing the Hg. salt.	Hg. present in soln.	Mercuric salt.	Direct weighing.	Decomposing the Hg. salt.
0.01180 g.	0.02967 g.	0.01184 g.	0.01185 g.	0.01034 g.	0.02590 g.	0.01032 g.	0.01038 g.
0.03540	0.08892	0.03543	0.03542	0.03102	0.07780	0.03100	0.03109
0.05900	0.1481	0.05903	0.05906	0.05170	0.12989	0.05175	0.05172
0.09440	0.23704	0.09444	0.09442	0.09306	0.2337	0.09308	0.09309

Estimation of Mercury (ous).—A stock solution was prepared by dissolving 7.5 g. of A.R. mercurous nitrate in water containing a little HNO_3 and it was made up to 250 cc. The mercury content of this solution was determined by titration with a standard 0.1*N*-KBr solution (Kolthoff and Larson, *J. Amer. Chem. Soc.*, 1934, **56**, 1881). An approximate 0.1*N* solution of mercurous perchlorate was prepared from extra pure red oxide of mercury by the action of perchloric acid and metallic mercury (Vogel, "A text-book of Quantitative Analysis", 1948, p. 315). The mercury content was similarly estimated with standard KBr solution.

From these solutions, a definite quantity was taken, diluted to 50 c.c. with water and mercury was precipitated in the same way, adding 0.5% solution of phenoxyacetic acid in the cold. A voluminous powdery white precipitate was formed, which settled quickly on keeping the solution on a hot water-bath for 10 minutes. The precipitation was complete, in this case also, between p_H 2 and 3. The precipitate was similarly filtered, washed, dried and weighed. The weight of mercury was calculated from the formula : $(PhO\text{-}CH^2\text{-}COO)_2Hg_2$. The mercurous salt was then decomposed and mercury estimated as sulphide, as before. During the decomposition of the salt by H_2O_2 etc. Hg (ous) was converted to the ic. (Found : Hg, 56.86. Calc. Hg : 56.98%). The results are shown in Table II.

TABLE II

Mercurous nitrate solution.				Mercurous perchlorate solution.			
		Mercury found by				Mercury found by	
Hg. present in soln.	Mercurous salt.	Direct weighing.	Decomposing the Hg salt.	Hg. present in soln.	Mercurous salt.	Direct weighing.	Decomposing the Hg salt.
0.01932 g.	0.03192 g.	0.01938 g.	0.01939 g.	0.01236 g.	0.02166 g.	0.01238 g.	0.01234 g.
0.03864	0.06566	0.03866	0.03868	0.02472	0.04322	0.02470	0.02471
0.05796	0.10139	0.05794	0.05793	0.04326	0.07574	0.04328	0.04321
0.07728	0.13515	0.07723	0.07725	0.06798	0.11887	0.06793	0.06794
				0.10124	0.17731	0.10132	0.10138

Separation of Mercury from Silver and Lead.—Mercury can be easily separated from silver and lead by precipitation with phenoxyacetic acid. Different quantities of lead nitrate and silver nitrate solutions, with known amounts of lead and silver in them, were mixed separately, with a definite volume of mercury salts. The p_H of the solution was raised to 3. Mercury was precipitated in the cold by the addition of the phenoxyacetic acid and the precipitate weighed, after washing and drying similarly. In the filtrate from the phenoxy-mercury salt, lead was estimated gravimetrically as $PbSO_4$ and silver as chloride. The results are shown in Table III.

TABLE III

Metals taken.		Phenoxy-Hg salt.	Metal found.	Metals taken.		Phenoxy-Hg salt.	Metal found.
		$Hg(NO_3)_2$				$Hg(ClO_4)_2$.	
Hg	0.04720 g.	0.11854 g.	0.04723 g.	Hg	0 05170 g.	0.12981 g.	0.05172 g.
Ag	0.0216	...	.0210	Ag	0.0216	...	0.0219
Hg	0.04720	.11859	.04725	Hg	0.05170	0.12991 g.	0.05176
Ag	0.0324	...	.0330	Ag	0.0432	...	0.0433
Hg	0.04720	.11864	.04727	Hg	0.05170	0.12989	0.05175
Ag	0.0432	...	.0438	Ag	0.0540	...	0.0541
Hg	0.04720	.11849	.04721	Hg	0.05170	0.12984	0.05173
Pb	0.04140	...	.04143	Pb	0.02070	...	0.02064
		$Hg_2(NO_3)_2$.				$Hg_2(ClO_4)_2$.	
Hg	0.05796	0.10138	0.05793	Hg	0.05562	0.09541	0.05561
Ag	0.0216	...	0.02190	Ag	0.0216	...	0.0215
Hg	0.05796	0.10143	0.05796	Hg	0.05562	0.09728	0.05559
Ag	0 0432	...	0.0430	Ag	0.0324	...	0.0322
Hg	0.05796	0.10136	0,05792	Hg	0.05562	0.09735	0.05563
Pb	0.04140	...	0.04148	Ag	0,0540	...	0.0546
Hg	0 05796	0 10143	0.05795	Hg	0.05562	0.09730	0 05560
Pb	0.05175	...	0.05170	Pb	0.02070	...	0.02063

The Nature of the Mercury Salt of the Phenoxyacetic Acid.—The mercuric salt of the phenoxyacetic acid is composed of silky white plate shaped crystals, m.p. 135°. It is soluble in hot water, and in all dilute acids, most readily in HNO_3. It is unstable to alkalies, giving yellow oxide of mercury. The mercurous salt is a powdery white substance (m.p. 178°), darkens above 130° and on exposure to air for a long time. It is insoluble in boiling water, but soluble in all acids. It is also unstable to alkalies and hydrogen sulphide.

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STUDIES ON THE VELOCITY OF FLOW OF SOLVENTS OF SOME HOMOLOGOUS SERIES THROUGH CHROMATOGRAPHIC COLUMNS IN RELATION TO THEIR VISCOSITY, HEIGHT OF THE COLUMN AND DENSITY

By D. R. Gupta and Abani K. Bhattacharya

The velocity of flow of a pure liquid through the adsorbent column is interestingly connected with the height of the column, density and viscosity of the liquid. The expression $Vh\eta/td$ is found to be constant for the members of homologous series. The value of the constant is different for different families.

The chromatographic method has assumed sufficient importance in separating the mixed constituents which could not be isolated otherwise. The method has been developed immensely on a qualitative basis, but much less quantitative work has so far been done in the study of the characteristics of the adsorbent columns and the structural role of the solvents.

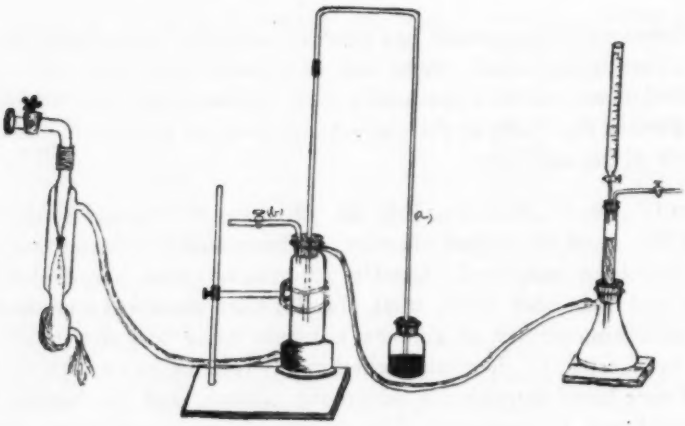
Wilson (*J. Amer. Chem. Soc.*, 1940, **62**, 1583), and Martin and Synge (*Biochem. J.*, 1941, **35**, 1358) have developed theories of chromatography and some quantitative work has also been published. Cassidy (*J. Amer. Chem. Soc.*, 1941, **63**, 2628) and Brockmann and Schodder (*Ber.*, 1941, **74**, 73) have suggested a method of standardising the adsorption affinity of alumina columns using azo dye mixtures. In this paper we have tried to determine whether any relation exists between the velocity of flow of a pure liquid through the adsorbent column, and its height, the density of the liquid and its viscosity. The results of our investigations appear to be interesting in that we get a constant value for the expression $Vh\eta/td$ for solvents belonging to a homologous family. Such an observation suggests that the flow of a solvent or solution is fundamentally connected with the structural characteristics of the molecules and specific adsorption affinity of the adsorbent. Experiments have been performed with four different homologous series (alcohols, ketones, esters and aromatic hydrocarbons).

Experimental

In determining the velocity of flow of the liquids through the columns, every care was taken to draw the liquid under a constant pressure inside the filter flask. The experiment was carried out at room temperature under uniform conditions of

surroundings. The pressure was reduced by running the filter pump connected to the tower, and the height of the mercury column in the tube (a) was kept at a fixed level by means of a control stop-cock (b) as shown in the figure. When the desired pressure inside the filter flask was attained, the constant flow of the liquid through the column was measured. The liquid was already filled in the chromatographic tube above the column up to the brim in which a burette was fitted by a rubber stopper. A stoppered side tube bent at right angle was also fitted through another bore of the rubber cork. While the liquid was flowing down the chromatographic tube, the empty space above the adsorbent was always kept full by slowly running the liquid into it from the burette. The side tube was used to remove air bubbles and to indicate uniform pressure on the liquid surface. The flow of the liquid

FIG. 1



down the column was so adjusted that the rate of flow from the burette was equal to the rate of flow of the liquid through the chromatographic column. It was then possible to determine the velosity of the liquid in the column by measuring the flow in c. c. per unit time from the readings of the burette. The state of constant flow of the liquid through the column was determined by counting the number of drops per unit time, when the same number of drops came out per minute. When this state of constancy was attained, the velocity of flow (V_c) was measured by dividing the total volume of the liquid which passed out from the burette by the time t, or in short, V_c = volume/time.

The height of the column was measured accurately by means of a cathetometer fitted with a vernier (least count = 0.002 cm.), the density of the liquid was determined by a pyknometer, and viscosity by an Ostwald viscometer. Having determined V_c, h, d and η, the values of the expression $Vh\eta/td$ were calculated in each case and these have been shown in the tables below.

TABLE I

Height of the mercury in the manometer=34.5 cm.
Temperature=22.0°. Adsorbent=$CaCO_3$.

Liquids.	Volume.	Time taken.	Height of the column.	Viscosity. $100 \times \eta$	Density.	$\frac{Vh}{t}$.	$\frac{Vh \times \eta}{t \times d} = k.$
MeOH	1 c. c.	200″	3.948 cm.	0.572	0.792	0.01974	0.01426
EtOH	1	339″	2.701	1.146	.789	.00/969	.01160
n-PrOH	1	729″	3.101	2.151	.8031	.0042°0	.01140
n-BuOH	1	803.5″	2.715	2.766	.8085	.00338	.01154
n-AmOH	1	1319″	2.892	4.425	.8220	.002188	.01180
MeAc	2.5	175″	3.450	0.372	.9268	.04928	.01977
EtAc	5	392″	3.251	.4410	.8962	.04147	.02088
n-Pr Ac.	2.5	270.5″	3.452	.5723	.882	.03190	.02071
n-BuAc	2.5	352″	3.345	.7912	.879	.02269	.02042
n-Am Ac	1.0	129″	2.752	.844	.870	.02133	.02070
Acetone	5	186″	3.640	.3301	.789	.09786	.04094
Methylethyl ketone	5	223.5″	3.508	.4200	.805	.07848	.04096
Benzene	5	88″	3.012	.6421	.878	.1712	.1251
Toluene	5	84″	3.125	.5802	.869	.1861	.1242
Xylene	5	105″	3.302	.6881	.8618	.1572	.1256

TABLE II

Adsorbent=alumina.

Liquids.	Volume.	Time.	Height of the column.	$100 \times \eta$.	Density.	$\frac{Vh}{t}$.	$\frac{Vh \times \eta}{d \times t} = k.$
MeOH	1 c. c.	128.5″	2.935 cm.	0.572	0.792	.02284	.01650
EtOH	2	527″	3.001	1.146	.789	.01139	.01654
n-PrOH	2	887″	2.750	2.151	.8031	.00626	.01666
n-BuOH	2.5	900″	2.649	2.766	.8085	.004794	.01640
n-AmOH	2.5	2611″	3.415	4.425	.822	.003270	.01660
Me Ac	1	129″	2.778	0.372	.9268	.02154	.008640
Et Ac	2	345″	3.019	.4410	.8962	.01750	.008614
n-Pr Ac	2.5	475″	2.525	.5723	.882	.01328	.008618
n-Bu Ac	3	884″	2.825	.7912	.879	.009585	.008628
n-Am Ac	2	675″	3.000	.844	.870	.0.889	.008624
Acetone	5	480.5″	3.274	.3301	.789	.03406	.01425
Methylethyl ketone	4	554.0″	3.3001	.4200	.805	.02708	.01420
Benzene	5	295″	2.756	.6421	.878	.04671	.03416
Toluene	3	175″	3.000	.5802	.869	.05142	.03434
Xylene	4	271″	2.950	.6881	.8618	.04354	.03443

Discussion

The value of Vh/t can be interpreted as related to the volume in c.c. which passes through 1 cm. of the column of a particular adsorbent per unit time. It appears that the value of Vh/t is connected specifically with the nature of the adsorbent, because the values of Vh/t are found to be different for the same solvent in $CaCO_3$ and alumina columns. This difference may be attributed to the surface characteristics of $CaCO_3$ and alumina and also to the fact that identical packing cannot be possibly guaranteed for the different materials.

Majority of separations had been suitably performed in chromatography when such solvents as benzene, acetone, methyl alcohol, or ethyl were used. It may be an interesting surmise to mention that the value of Vh/t may directly give us a clue for the liquid being used as a suitable solvent when passed through a particular adsorbent column, provided the value of 'h' could be kept constant for the different solvents. But our attempts have been so far in vain to pack up the adsorbent up to a constant height in every case. Experiments are in progress to evolve a method of filling up the columns having a constant height.

It is interesting to note that $Vh\eta/td$ happens to be constant for the same family of compounds, and from this it may be concluded that the flow of liquid through the adsorbent columns is fundamentally governed by the structural characteristics, or, in other words, the functional group or groups in the molecule of the liquid. The liquid, when it is flowing through the capillaries of the column, appears to be oriented to the surface as it to passes. This orientation would depend upon the functional group characteristics of the molecules. The constancy of the value of $Vh\eta/dt$ may serve as a quantitative basis of evidence in favour of the view that surface properties of adsorbent columns are appreciably influenced by the structure of the solvent as well as that of the solute. Experiments are in progress to determine the usefulness of the constant, $Vh\eta/dt$ in studying the nature of the adsorbent columns generally used in chromatography.

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